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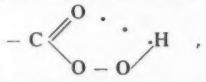
A SPECTROSCOPIC STUDY OF HYDROGEN BONDING IN PERFORMIC AND PERACETIC ACIDS[1]

BY PAUL A. GIGUÈRE AND A. WEINGARTSHOFER OLMOS

ABSTRACT

The infrared spectra of concentrated performic and peracetic acids were measured in the rock-salt region. The most significant features are the O–H stretching frequency at 3310–3350 cm.$^{-1}$ and the OH bending frequency at 1450 cm.$^{-1}$ which, for both peracids, remain essentially the same in the vapor state as in the liquid or in solution in nonpolar solvents. This is attributed to intramolecular hydrogen bonds resulting in particularly stable five-membered rings,



Steric conditions in the percarboxylic group are favorable to such ring formation or *chelation*. From the observed frequency shifts the energy of these hydrogen bonds is estimated to be about 7 kcal. per mole. No evidence for unchelated molecules was found even in very dilute solutions of peracetic acid in nonpolar solvent nor in the vapor at low pressure and moderate temperature. Tentative assignments of the other frequencies in the spectra of the peracids are made by comparison with those of formic and acetic acids.

The danger involved in handling these peracids in concentrated form is emphasized.

The aliphatic acids react with concentrated hydrogen peroxide to form the corresponding peracids, RCOOOH. The lower peracids have assumed new importance of late because of their use as oxidizing and hydroxylating agents in the preparation of certain classes of organic compounds. For a review cf. Swern (22). Because of the unusual molecular association of the lower carboxylic acids, due to formation of double molecules stable even in the vapor state, it was of interest to investigate the nature of hydrogen bonds in the corresponding peracids. Infrared spectroscopy was the ideal tool for that purpose especially in view of the chemical unstability of these compounds. As could have been predicted from structural considerations the molecules of peracids show no tendency to dimerize; instead intramolecular hydrogen bonds are formed exclusively in the vapor as well as in condensed phases.

EXPERIMENTAL

Peracetic acid was studied first because it is less unstable than performic acid and its properties are better known. The preparation was done after the method of d'Ans and Frey (5). One mole of acetic anhydride (Merck's 97%) was mixed

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Contribution from the Chemistry Department, Laval University, Quebec, Que., with financial assistance from the National Research Council of Canada.

with two moles of 99% hydrogen peroxide (produced from Becco's 90% solution) and 1% concentrated sulphuric acid acting as a catalyst. After distillation at 35–40°C. under reduced pressure (20 mm. Hg) using a 60 cm. Vigreux column, the distillate contained 89% peracetic acid. Further concentration up to 95% was attained after three successive distillations. Beyond that point fractional crystallization was resorted to, although the efficiency of that method was very low, indeed. A product 97% pure was finally used for recording the spectrum as the remaining impurities, mostly water and acetic acid, caused no serious difficulty in that respect. Obtainment of a purer product would have required rather large amounts of material. The peracid was analyzed by titration with potassium iodide (5). At the temperature at which the spectrum was recorded, 25°C., decomposition of peracetic acid was found to be negligible. The pressure in the absorption cell never increased noticeably during a run, nor did the intensity of the absorption bands of CO_2 which is known to be formed in the reaction along with some formic and glycolic acids (15).

The method of d'Ans and Kneip (6) was followed for preparing some performic acid: a mixture of 20 gm. of 99% formic acid (Merck's) with 25 gm. of hydrogen peroxide of the same concentration, and 6.5 gm. of sulphuric acid was allowed to reach equilibrium at ordinary temperature. This took a couple of hours, after which the mixture was distilled at about 30° under 5 mm. Hg; the distillate consisted of some 10 gm. of 85% performic acid. Because of the risk involved in that operation great care was always taken. Unfortunately, in one last attempt to obtain a more concentrated product by distilling a smaller fraction of the mixture, an explosion occurred *after the distillation*, injuring the operator. Details of this accident have been reported elsewhere (25). D'Ans and Kneip, who succeeded in preparing a product 90% pure, claimed that only certain classes of catalysts could initiate detonation. Certainly none of these were present in our case. Therefore, users of performic acid should beware of the potential danger in handling it when it is concentrated.

Since the spontaneous decomposition of performic acid is appreciable even at 0°C. a fresh sample had to be prepared for recording each spectrum; for the same reason the absorption cell was evacuated after each run. Judging from the spectra, formic acid was the main product of decomposition; this caused some difficulty in interpreting the data, as explained below. On the other hand, the explosive reaction presumably yields water and carbon dioxide,

$$HCOOOH = H_2O + CO_2.$$

The spectra were recorded with a Perkin-Elmer 12 C infrared spectrometer; a rock-salt prism was generally used except in a few runs where an LiF prism was needed for greater resolution in the 3μ region. The absorption cell for vapors was an 11 cm. glass tube with rock-salt windows held tight by means of Koroseal gaskets. The liquid sample was contained in a side tube at about 10° lower than the cell itself to prevent fogging of the windows. For the spectra of the liquids one drop was pressed between two silver chloride plates as rock salt is attacked by the peracids. The conditions under which the various spectra were recorded

are given in each case (Tables I and II). The vapor pressure of the peracids in the absorption cell could not be measured exactly; the figures given are only rough estimates (from temperature of the sample) specially in the case of performic acid. For comparison purposes the spectra of formic and acetic acids, 99% pure, were recorded under conditions where either the monomer or the dimer are strongly predominant. The relative concentration of either form was estimated from existing dissociation data (4, 20).

DISCUSSION OF RESULTS

Tracings of the infrared spectra of the peracids and the corresponding carboxylic acids are shown in Figs. 1 and 2; the frequencies of the principal bands are

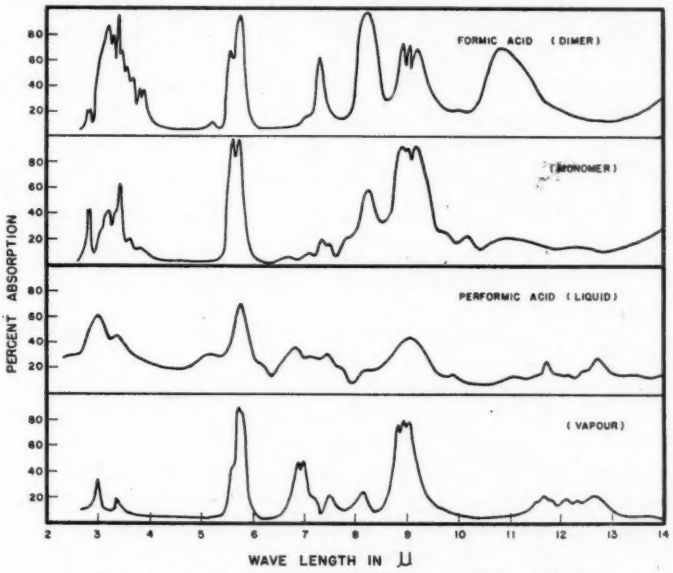

FIG. 1. Infrared spectrum of formic and performic acids. .

listed in Tables I and II together with the proposed assignments. As may be seen the O–H stretching frequency at 3μ in the peracids remains essentially unchanged on going from the liquid to the vapor. Obviously the bands are much broader in the former case, owing to intermolecular perturbations, but the maximum occurs at the same frequency as the sharp band in the vapor. Therefore, the hydrogen atom must be bound the same way in both physical states.

A fair idea of the probable configuration of the percarboxylic group may be had a priori from consideration of the structure of aliphatic acids and peroxides. The bond lengths and angles assumed on that basis reveal a situation favorable to formation of intramolecular hydrogen bonds, as shown in Fig. 3. Here the C=O and C−O bond lengths are the same as in formic acid, from spectroscopic, X-ray, and electron diffraction data (8); Badger's rule applied to the

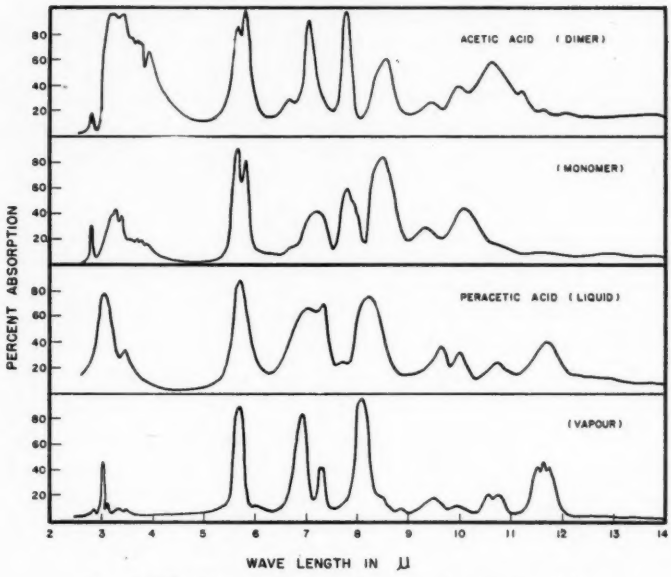

FIG. 2. Vibrational spectrum of acetic and peracetic acids.

3310 cm.$^{-1}$ frequency gives 1.02 Å for the O—H distance as against 1.07 Å in acetic acid (21). If the O—O—H bond angle is made 100°, a decrease of some 5° from that in hydrogen peroxide, to account for the replacement of a hydrogen atom by an electronegative group (this estimate may yet be too conservative), then the hydrogen bond length O · · · H turns out to be about the same as in water and alcohols, 1.78 Å, (21) on the assumption that the chelate ring is planar. The present spectroscopic data are not sufficient to decide on this latter point; in the accepted configuration of hydrogen peroxide the two OH groups lie in planes at right angles, or thereabout, to each other (11). However, the electrostatic attraction of the carbonyl oxygen for the hydrogen atom is undoubtedly sufficient to overcome most, if not all, of the potential barrier (4–5 kcal. per mole) restricting rotation about the O—O bond (10). At any rate, whether the chelate ring is planar or slightly puckered the hydrogen bond length seems to be of the right order for a particularly strong bond.

Indeed, all indications are to the effect that in the peracids the chelate ring is not easily broken. The very weak absorption at 3600 cm.$^{-1}$ (corresponding to the unperturbed O—H vibration), which appeared in the spectrum of both peracids, was certainly due to the few per cent of carboxylic acids remaining in the samples as proved by temperature and dilution studies. Because of the thermal unstability of these compounds it was not feasible to study extensively the temperature effect. Peracetic acid vapor was heated up to 42° and the partial pressure reduced to 6 mm. Hg without any effect on the O—H absorption band. Similarly, dilution, more than one-hundredfold, from the saturation concentration in

TABLE I

INFRARED ABSORPTION BANDS OF FORMIC AND PERFORMIC ACIDS (FREQUENCIES IN CM.$^{-1}$)

Formic acid		Performic acid		
Monomer†	Dimer††	Vapor†††	Liquid	Assignment
3597, 3558 (s.)		3590 (v.w.)	3590 (v.w.)	ν(O–H) free
		3367, 3340 (w.)	3378 (s.)	ν(O–H) bound
	3194			(2600 + 660)
	3144 (v.s.)			
	3114			(1780 + 1360)
	3029			(1740 + 1360)
2958 (v.s.)	2957 (v.s.)	2987, 2967 (w.)	2941 (M.)	ν(C–H)
	2899			(1740 + 1213)
	2822			(1740 + 1108)
	2741			
	2622			(1780 + 925)
	2582			(1740 + 925)
	1920 (w.)			
1780 (v.s.)				
1740 (v.s.)	1780, 1740 (v.s.)	1748, 1739, 1730 (v.s.)	1739 (v.s.)	ν(C=O)
		1453, 1432 (s.)	1455 (s.)	δ(OH) bound
	1360 (s.)	1340 (w.)	1351 (w.)	
1213 (s.)	1213 (v.s.)	1243 (w.)	1240 (v.w.)	δ(OH) free, and ν(C–O)(?)
1123, 1108, 1090 (v.s.)	1117, 1103, 1086 (v.s.)	1135, 1122, 1106 (v.s.)	1111 (v.s.)	δ(CH)(?)
1033 (w.)				
		872, 859, 842 (w.)	855 (w.)	ν(O–O)
		825, 810, 795 (w.)	782 (m.)	
658 (s.)	660 (s.)			

	†	††	†††
Source temp. (°C.)	10	10	15
Cell temp. (°C.)	115	24	25
Pressure (mm. Hg)	16	16	30 (?)
% Dissociation	95	15	—

carbon tetrachloride (0.44 M), resulted in complete disappearance of the weak maximum at 3600 cm.$^{-1}$ (Fig. 4) even with increased sample thickness. At the same time the absorption coefficient of the 3310 cm.$^{-1}$ band remained independent of concentration. In the carboxylic acids the same conditions would have

TABLE II

INFRARED ABSORPTION BANDS OF ACETIC AND PERACETIC ACIDS (FREQUENCIES IN CM.$^{-1}$)

Acetic acid		Peracetic acid		
Monomer†	Dimer††	Vapor†††	Liquid	Assignment
		5180 (?) (v.w.)		(1750 × 3)
		4710 (v.w.)	4670 (v.w.)	(3310 + 1440)
			4430 (v.w.)	(3310 + 1210)
			4350 (v.w.)	
			4240 (v.w.)	(3310 + 1040)
			4160 (v.w.)	(3310 + 930)
			4040 (v.w.)	(3310 + 858)
3570 (m.)		3570 (v.w.)		ν(O−H) free
		3310 (w.)	3310 (v.s.)	ν(O−H) bound
3140	3140	3140 (v.w.)		ν(O−H) bound
3085	3085 (v.s.)	3080 (v.w.)		(1760 + 1370)
3050	3050	3025 (v.w.)		
2980 (m.)	2980 (v.s.)	2900 (v.w.)	2920 (m.)	ν(C−H)
2870	2870			
2800	2800			(1760 + 1230)
2710 (w.)	2710 (w.)			
2645 (w.)	2645 (w.)			
2570 (w.)	2570 (w.)			
1794, 1772 (v.s.)	1770 (v.s.)			
		1760 (v.s.)	1750 (v.s.)	ν(C=O)
1730 (v.s.)	1740 (v.s.)			
	1505 (w.)			
1410 (s.)	1420 (v.s.)	1450, 1439 (v.s.)	1440 (v.s.)	δ(OH) bound
1380 (v.w.)	1365 (v.w.)(?)	1382, 1371 (s.)	1370 (v.s.)	δ(CH) (?)
		1248		
1285 (s.)	1290 (v.s.)	1239, 1229 (v.s.)	1210 (v.s.)	ν(C−O) (?)
1168 (v.s.)	1170 (s.)			
	1060 (w.)	1050 (v.w.)	1040 (m.)	
1007 (w.)	1007 (m.)	1010 (v.w.)	1000 (m.)	
976 (v.w.)	943 (s.)	948, 933 (m.)	930 (m.)	
	894 (w.)			
		868, 861, 853 (v.s.)	858 (s.)	ν(O−O)
		656 (?)		
		648 (?)		

	†	††	†††
Source temp. (°C.)	20	20	14
Cell temp. (°C.)	100	40	24
Pressure (mm. Hg)	11.7	11.7	6 (?)
% Dissociation	87	15	—

resulted in considerable increase of the "free" O−H absorption band at the expense of that due to the hydrogen bond.

Numerous examples of intramolecular hydrogen bonding have been reported in the literature; well-known examples are the *o*-substituted phenols (21). The

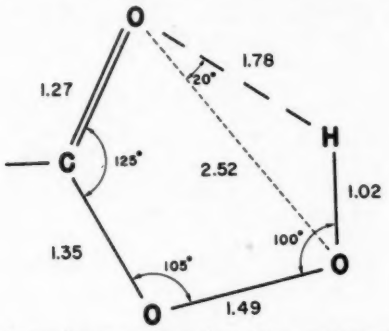

FIG. 3. Approximate configuration of the percarboxyl group.

case of the peracids is different, in that there is no aromatic ring to stabilize the chelate structure and, furthermore, the hydrogen atom is located at the end of a chain of three single bonds with two degrees of rotational freedom. The remarkable stability for the chelate structure is no doubt due to specially favorable steric conditions rather than to the strength of the hydrogen bond itself. A rough estimate based on Badger's relationship between O—H frequency shift and hydrogen bond energy (1) leads to values of 6 and 7 kcal. per mole respectively for performic and peracetic acids. This is about the same as in alcohols and somewhat lower than in carboxylic acids (21). Although the latter have slightly stronger hydrogen bonds than the corresponding peracids their chelate ring is obviously much less stable because it contains two hydrogen bonds. As indicated by the absence of any absorption in the region around 3100 cm.$^{-1}$ peracids show

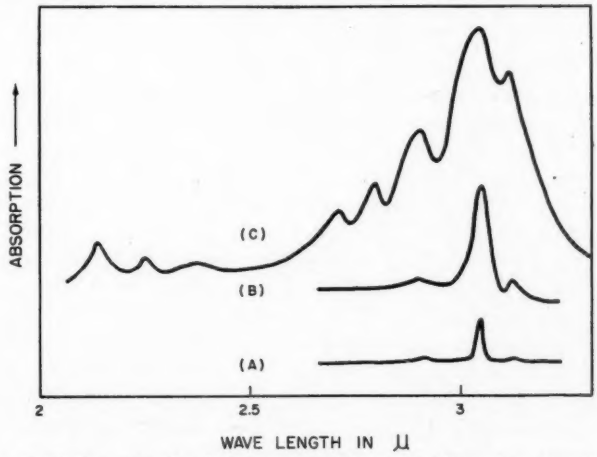

FIG. 4. O–H absorption band of peracetic acid dissolved in carbon tetrachloride.

	Concentration	Sample thickness
(*A*)	0.0037 *M.*	5.7 mm.
(*B*)	0.037 *M.*	0.85 mm.
(*C*)	0.44 *M.*	0.85 mm.

no tendency to form double molecules, which is easily understood, since these would involve 10-membered rings for which no appreciable stability can be imagined.

Like the O—H stretching mode the OH bending is expected to be strongly affected by internal hydrogen bonding. This effect has not been much investigated so far because of interference of other bending and stretching vibrations occurring in the same region. Peracids show a remarkably strong absorption band around 1450 cm.$^{-1}$, corresponding, undoubtedly, to the OH bending mode. No other assignment could fit this frequency which is absent in the spectrum of formic acid. In the latter this vibration is believed to occur at 1213 cm.$^{-1}$ in the monomer and at 1360 cm.$^{-1}$ in the dimer. A priori the higher frequency in the peracids seems surprising; however, it may be accounted for by the fact that the hydrogen atom does not lie on a straight line between the two oxygen atoms but rather at an angle of about 20° (Fig. 3). As a result the interaction of the carbonyl oxygen on the hydrogen atom is expected to be greater for the OH bending vibration and lesser for the O—H stretching; the corresponding frequency shifts should be affected accordingly as is, indeed, observed by comparison with the carboxylic acids, where the O—H · · · O group is linear. Incidentally, these steric factors must have some bearing on any relationship between hydrogen bond energy and observed frequency shift, at least in chelate compounds. Recently Davison (9), while studying the effect of hydrogen bonding on the characteristic carbonyl frequencies, found that in perbenzoic acid there was no evidence for monomer–dimer molecules; he attributed to intramolecular hydrogen bonds the presence of a single O—H absorption band at 3250 cm.$^{-1}$ (as compared with 3550 cm.$^{-1}$ for the monomer of benzoic acid). This also confirms the fact that in peracids, RCOOOH, as in carboxylic acids, the O—H stretching frequency decreases as *R* becomes more complex.

Chelation through intramolecular hydrogen bonds is reflected in the physicochemical properties of the peracids. No data are available on the vapor pressure of performic acid but from its behavior in fractional distillation it is known to be more volatile than formic acid. As for peracetic acid, it boils at 105°, 13 degrees lower than acetic acid, in spite of a higher molecular weight (22). For the same reason it may be predicted that the entropy of vaporization of the peracids is near the value of Trouton's constant, 21 cal. per mole per deg. The greater chemical unstability of the peracids may be indicative of a weaker O—O bond than in hydrogen peroxide. One might attribute the weakening of the peroxide bond to the twisting away from the stable skew configuration. Still, there are certainly other important factors to be considered in that connection such as, for instance, the electron shift towards the peroxide bond previously discussed by Walsh (24).

Assignment of the other frequencies in the spectrum of both peracids was attempted by comparison with those of the corresponding carboxylic acids. Unfortunately the latter have not yet been accounted for satisfactorily, even in the simple case of monomeric formic acid, despite numerous investigations of the normal and deuterated acids (2, 3, 7, 12, 13, 14, 16, 17, 18, 19, 26). First, the C—H stretching vibration around 2950 cm.$^{-1}$ in performic acid is quite similar

to that in the monomer of formic acid. In the dimer this band is submerged in the broad O−H stretching band; this is in contrast with the peracids when it is clearly resolved, even in the spectrum of the liquid. There is no doubt regarding the C−O frequency at 1740 cm.$^{-1}$ which resembles closely that in the dimers of carboxylic acids. In the monomers it is split into a doublet in the vapor (7) as well as in solution (23). (The peaks at 1780 and 1790 cm.$^{-1}$ in the spectra of formic and acetic dimers (Figs. 1 and 2) are due to some 15% of the monomer present.) The O−O vibration is unequivocally attributed to the 860 cm.$^{-1}$ frequency, a value some 2−3% lower than in hydrogen peroxide (10).

The remaining stretching frequency, namely C−O, is the subject of much uncertainty in the peracids as well as in the carboxylic acids. Previously it has been attributed to the 1100 cm.$^{-1}$ band in formic acid (19) and then to the 1380 cm.$^{-1}$ band in acetic acid (7, 13). The former assignment is now ruled out because the 1100 cm.$^{-1}$ band shows not only the same frequency, but also the same contour in performic as in formic acids. Normally one would expect the C−O vibration to be shifted to an appreciably lower frequency in performic acid due to substitution of an OH group for a hydrogen atom; in fact a slight shift in the opposite direction is observed. Another serious objection to the above assignment is the absence of any absorption around 1100 cm.$^{-1}$ in acetic as well as in peracetic acids. For these various reasons the 1100 cm.$^{-1}$ band is believed to be due to the CH bending mode in performic and formic acids. On the other hand the 1380 cm.$^{-1}$ band in acetic acid cannot very well correspond to the C−O vibration since there is no trace of it in formic acid. Herman and Hofstadter (17) had reached the same conclusion from their study of deuterated acetic acid. Tentatively it is concluded that the C−O vibration is accidentally degenerate with either the 1100 cm.$^{-1}$ or the 1213 cm.$^{-1}$ vibrations. This latter frequency has until now been identified with the "free" OH bending mode in carboxylic acids. This explanation cannot be complete because of the fact that the 1213 cm.$^{-1}$ band in formic acid is equally strong, if not stronger, in the spectrum of the dimer; it is still quite prominent in very dilute carbon tetrachloride solutions estimated to contain only 3% of the monomer (23). There is also the possibility of Fermi resonance with the first overtone of the frequency at 660 cm.$^{-1}$

The absence of any absorption at 1030 cm.$^{-1}$ in performic acid seems to rule out the assignment of that frequency to the CH bending mode, as suggested by Thomas (23). Finally the origin of the weak maxima at 1240 and 1340 cm.$^{-1}$ in performic acid remains doubtful. They appear too weak for fundamental vibrations; rather it is believed that they are due to the 15% formic acid present in the sample of peracid used. In view of the uncertain situation in performic acid no attempt was made to decipher the more complex spectrum of peracetic acid besides identification of the bands involved directly in hydrogen bond formation.

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fellowships to one of them (A.W.O.). The helpful cooperation of the Buffalo Electro-Chemical Co. is also acknowledged.

RÉSUMÉ

La formation de liaisons hydrogène dans les acides performique et peracétique a été étudiée par spectroscopie infrarouge. Contrairement aux acides gras (formique, acétique, etc.) qui sont associés en molécules doubles grâce à des liaisons hydrogène particulièrement fortes, les peracides ne forment que des liaisons intramoléculaires. Ce phénomène, dit de chélation, se manifeste par l'invariance des fréquences de vibration du groupe OH lorsqu'on passe du liquide à la vapeur ou inversément. La configuration du groupe COOOH se prête bien à la formation de liaisons hydrogène internes et les anneaux qui en résultent subsistent même à basse pression de vapeur ou en solution très diluée. L'énergie de ces liaisons hydrogène est évaluée à environ 7 kcal. per mole d'après les décalages de fréquence observés. Par comparaison avec les spectres des acides formique et acétique on a attribué les principales bandes d'absorption aux divers modes de vibration des peracides correspondants.

Les peracides concentrés sont des explosifs dangereux.

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THE SIZE AND SHAPE OF LYSOZYME[1]

By J. Ross Colvin

ABSTRACT

The molecular weight of lysozyme has been redetermined by the ultracentrifuge as 14,100 ± 500. The molecule appears to be a stubby prolate ellipsoid of rotation, with a maximum length of 90 Å and a minimum equatorial diameter of about 18 Å depending on the degree of hydration assumed. Alternative possibilities of chain orientation within this shape are discussed assuming that the chains are coiled in Pauling–Corey helices.

INTRODUCTION

In a recent review, Gutfreund has emphasized the need for more accurate data about the molecular constants of even the commoner proteins (11). His point is well illustrated by Fevold's valuable survey of the egg proteins (8) in which the published estimates of the molecular weight of lysozyme range from 13,900 to 18,000. Furthermore, the most precise estimate of 13,900 ± 600 from X-ray measurements is significantly lower than other determinations by osmotic pressure, ultracentrifuge, or analytical methods, although some of these depend on undetermined parameters such as the partial specific volume (1). For this reason, the molecular weight and shape of lysozyme have been carefully redetermined in the ultracentrifuge.

MATERIALS AND METHODS

Three samples of crystallized lysozyme from Armour and Co., Chicago, were included in the study. Except for minor differences in moisture content, as estimated by drying *in vacuo* at 100° for 16 hr., the samples were identical. Microscopically they were composed of thin clear platelets of irregular shape which dissolved rapidly in distilled water to give a solution of pH 5.4. Such solutions were perfectly clear, without visible contamination. Similar solutions in 0.05 *M* phosphate buffer, pH 6.8, were homogeneous electrophoretically (6) and in the ultracentrifuge. Fitting a normal Gaussian function to the diffusion curves showed samples to be monodisperse on a mass basis. Chloride content of the crystals was less than 0.4% as estimated by the method of Conway (7). Nitrogen percentage was 18.6 ± 0.1 by micro-Kjeldahl. Finally, the material was visibly active against *Micrococcus lysodeikticus* in very dilute solutions although no quantitative estimates of activity were undertaken.

In all determinations, the buffer was 0.05 *M* phosphate, pH 6.8, made according to Clark (4) from reagent grade materials. Since the specific conductivity of a 0.5% solution of lysozyme in the buffer differed by less than 1.2% from that of the pure buffer, the ionic strength (0.1) was assumed to be sufficient to suppress electrostatic interaction.

Sedimentation constants were determined in a Spinco Model E electrically

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driven ultracentrifuge at 250,000 gravities. Boundary displacements were estimated directly from the plates by a microcomparator to ± 0.001 mm. Sedimentation constants were estimated directly from these boundary displacements in the usual manner, since the magnitude of other errors made the more refined technique of Cecil and Ogston (2) superfluous. Measured sedimentation constants were corrected to 20°C. in water by the usual methods (21).

Partial specific volume of lysozyme was estimated by the method of intercepts (12).

Diffusion coefficients were estimated by supporting a Claesson type cell (3) in the thermostat of a standard Tiselius electrophoretic apparatus in such a way that two diffusions could be conducted simultaneously. Previous checking of the apparatus gave accurate, reproducible estimates of the diffusion coefficient of sucrose. Refractive index gradients were recorded by the schlieren method (13) and diffusion coefficients calculated by the method of moments (14). Times of diffusion varied between 20 and 27 hr. All determinations were conducted at 29.55° ± 0.02°C. but values were adjusted to 20°C. in water by the usual methods (19).

RESULTS

Five determinations of the sedimentation constant $s_{w,20}$ of lysozyme, at varying concentrations, are shown in Table I. Clearly $s_{w,20}$ is independent of concentration in this range. The mean value $1.87 \pm 0.02 \times 10^{-13}$ is in good agreement with the earlier estimate, 1.9×10^{-13} obtained by Oncley and Brown, as cited in Alderton *et al.* (1).

TABLE I

SEDIMENTATION CONSTANT OF LYSOZYME AT VARYING CONCENTRATIONS

Concentration, %	$s_{w,20} \times 10^{13}$
0.3	1.84
0.4	1.82
0.5	1.90
0.6	1.86
0.8	1.91
	Mean 1.87 ± 0.02

Eight independent determinations of the partial specific volume of lysozyme at 25°C. yielded the value 0.688 ± 0.007. It was assumed that the change in this parameter over a 5° interval was negligible. The estimate was also independent of concentration from 0 to 0.9%. This value is considerably lower than the range assumed by Oncley and Brown in Alderton *et al.* (1) and is much lower than that for most proteins. However, it is consistent with the very high arginine and aspartic acid content of lysozyme (5, 10).

Six determinations of the diffusion coefficient of lysozyme as a function of concentration are shown in Table II, corrected to 20°C. in water. Clearly, the coefficient is independent of protein concentration within this range. Its mean

TABLE II
DIFFUSION COEFFICIENT OF LYSOZYME AT VARYING CONCENTRATIONS

Concentration, %	$D_{w,20} \times 10^7$, cm.²/sec.
0.30	10.7
0.39	10.1
0.57	10.6
0.66	10.2
0.74	10.5
0.80	10.5
	Mean 10.4 ± 0.1

value, 10.4 ± 0.1 $\times 10^{-7}$ cm.² per sec., is considerably lower than the previous estimate of 11.2 $\times 10^{-7}$ cm.² per sec. by Oncley and Brown (1) but since no limits of error are indicated for their determination, comparison is difficult. In contrast, this value of the coefficient is much higher than the figure of 8.6 $\times 10^{-7}$ found by Passynsky and Plaskeyev (16) from three experiments of very short duration. Since the latter investigation was of preliminary character on uncharacterized material, it is believed that the sample may have been contaminated with substances of higher molecular weight. The extensive dialysis used to purify their solutions would tend to concentrate such fragments in the sample.

Since the density of buffer was 1.00289, application of the usual formula for sedimentation velocity, $M = RTs/D(1 - V\rho)$, gave the molecular weight of lysozyme as 14,100 ± 500.

Assuming this value of the molecular weight, the frictional ratio f/f_0 was estimated in the usual way (21) as 1.3 ± 0.2. Perrin's formula (18) for an unhydrated ellipsoid of rotation then gave an axial ratio of 5. This is widely different from the only previous explicit estimate of 11 (16) but this was based on a questionable extrapolation of an empirical formula involving viscosity data. From the axial ratio found here and the partial molar volume of lysozyme, the length of the lysozyme molecule was estimated as approximately 90 Å and its maximum breadth as about 18 Å. If 50% hydration of the molecule is assumed, the axial ratio becomes 2.5 and the corresponding length and breadth of the molecule are about 60 Å and 24 Å respectively. Patently, the assumptions made in the theory and the limits of error of the data are such that these dimensions must not be regarded as more than approximate estimates.

DISCUSSION

The molecular weight found here is in excellent agreement with that found from X-ray data by Palmer, Ballantyne, and Galvin (15). It also agrees with the less definite estimate of Oncley and Brown cited in Alderton *et al.* (1) assuming lower values of the partial specific volume. Estimates of molecular weight from amino acid composition data are a little higher than the value found here but there is reason to think that the analytical values for some residues may be high (8). Accordingly, this investigation puts lysozyme in that small class of proteins the molecular weights of which have been determined accurately and precisely by two or more independent methods.

It is interesting to speculate on the possible arrangement of the polypeptide chains within this small protein in solution. Assuming the Pauling–Corey picture of stable polypeptide helices (17) and either one or two chains per lysozyme molecule (8, 9, 20), the 120 amino acid residues may be fitted into the approximate shape suggested for the anhydrous protein, in three ways. First, if there are 3.7 residues per turn in a single chain for lysozyme and the helix is folded back once at its midpoint, from Pauling and Corey's measurements (17), this model would accommodate about 125 residues. Second, the same number would be held by two chains in two parallel helices of similar structure although data from reduction and alkylation of the disulphide bridges (9) as well as from free amino groups (20) make this structure unlikely. Finally, if the folding is of the 5.1 residues per turn type, the estimated diameter of the coil would also be close to 18 Å and a unit 90 Å long would accommodate approximately 100 residues. Although agreement seems to be less satisfactory for this possibility than in the prior models, the errors in estimation of shape are such that the differences may not be significant. Similar structures may also be postulated for the 50% hydrated model but are not very convincing because of the errors inherent in the theory. However, experimental attempts to differentiate between these alternatives are now under way.

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ADDITION COMPOUNDS OF THE GROUP IV HALIDES

I. TRIETHYLAMINE AND THE TETRACHLORIDES OF SILICON, GERMANIUM, TIN, AND TITANIUM[1]

By W. R. Trost

ABSTRACT

Compounds with the composition of tetraminates were prepared from the tetrachlorides of silicon, germanium, tin, and titanium with triethylamine. Thermal decomposition of the tetraminates leads to the suggestion that they are molecular addition compounds.

The existence of complex 'addition' compounds involving some group IV tetrahalides has been known for many years. Although these compounds present a specific challenge to valence theory, their existence has not been emphasized but rather seems to have been ignored or forgotten until recent time. Of the group IV*b* tetrachlorides (carbon, silicon, germanium, tin, lead), lead (5) and particularly tin (6) are known to form a variety of addition compounds with donor groups like ethers, ketones, aldehydes, and amines. Compound formation between silicon tetrachloride and pyridine, $SiCl_4 \cdot 2Pyr$, was reported in 1887 (1), and between triethylamine and germanium tetraiodide in 1933 (3).

But much greater interest has been shown in the substitution reactions that silicon and germanium tetrahalides undergo, to form covalent compounds, than has been directed to addition type reactions that may simultaneously occur. The best condition for substitution, and that generally studied, occurs when the donor group is associated with reactive hydrogens. In this situation addition reactions can become obscured or even remain unnoticed. But when attention is focused on addition rather than on substitution, and conditions favorable to the formation of addition compounds are established, then evidence for such compounds can be discovered in the reactions of silicon tetrachloride with donor groups like aldehydes, ketones, and especially amines (10).

The remaining member of the group, carbon tetrachloride, does not easily engage in substitution reactions, nor is it by any means so adept at addition as are the heavier members of the family. However freezing point investigations have provided evidence for what seem to be definite, though low temperature, associations between carbon tetrachloride and pyridine (4).

The group IV*a* elements (titanium, zirconium, hafnium) could be expected to form complex compounds from their tetrahalides, for valence theory assigns to these atoms vacant *d* and *p* orbitals that can be used in conjunction with the donor electron pairs to establish orthodox coordinate bonds. Examples of known addition compounds are, however, rather limited, but the tetrachlorides of titanium and zirconium have recently been shown to be able to form compounds with organic esters (2).

The group IV*b* tetrahalides are saturated molecules in the sense that all orbitals

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and electrons in the valence group are fully engaged. This is in contrast to the group IV*a* tetrahalides, which still retain five vacant orbitals similar in stability to those utilized in the covalent bonding. If the valence orbitals are called '*n*' type orbitals, then the group IV*a* tetrahalides will be able to form addition compounds with *n* type orbitals. But the group IV*b* tetrahalides must use $n + 1$ type orbitals, external to the valence group, if the additionlike compounds are to be interpreted in terms of coordinations (8).

Two questions of interest arise then, in regard to these compounds. First of all, are the addition compounds formed by the group IV*b* elements to be taken seriously as coordination compounds? If they are coordination compounds, the utilization of $n + 1$ type orbitals must also be taken seriously, with some general consequences in the fields of intermolecular forces, and of the structures of active complexes. Secondly, is there a distinctive difference between the addition compounds of the group IV*b* and the group IV*a* elements, corresponding to their different electron structures? With these particular problems in mind, some reactions of silicon, germanium, tin, and titanium tetrachlorides with triethylamine, and with ethylamine (11), were undertaken, and the results are presented and discussed below.

EXPERIMENTAL

Four tetrachlorides (silicon, germanium, tin, titanium) were each mixed with triethylamine under two different sets of conditions. In one series the compounds were prepared in vacuum with no solvent. In the other series reaction was effected in an anhydrous solvent in an atmosphere of dried nitrogen.

Vacuum Preparations

The amine and the tetrachloride were each prepared for use by two successive fractionations within the vacuum system. Known volumes of the purified liquids were condensed into a bulb at − 78°C., with the amine in 8/1 molar excess. The mixture was slowly warmed to room temperature while being magnetically stirred. All products volatile at 20°C. were pumped off and the dry products weighed and analyzed. The yields and compositions of the products are presented in Table I.

TABLE I

PREPARATIONS IN VACUUM
TRIETHYLAMINE AND GROUP IV TETRACHLORIDES

Tetrachloride	Product	Yield, %
$SiCl_4$	$SiCl_4.4NEt_3$	27
$GeCl_4$		8
$SnCl_4$	$SnCl_4.2NEt_3$	87
$TiCl_4$	$2TiCl_4.NEt_3$	80

The following observations on the vacuum preparations were thought to be significant. The mixtures of the amine with the tetrachlorides of silicon, germanium, and tin were white suspensions at low temperatures, with some yellow coloration that faded on warming in the case of silicon and germanium, but

that became more extensive with time in the case of tin. Upon evaporation a white powder with the approximate composition, $SiCl_4 . 4NEt_3$, (Exp. Si, 4.7%; amine/Cl ratio, 1.06. Theor. Si, 4.9%; amine/Cl ratio, 1.00) was recovered from the silicon preparation. The germanium compound, in the process of evaporation, partly reverted to a yellow oily material that appeared as a contaminant in the white powder. The yield, Table I, was calculated in terms of a tetraminate. The tin compound was recovered as a yellow diaminate, $SnCl_4 . 2NEt_3$ (Exp. Cl, 35.5%; NEt_3, 42.8%. Theor. Cl, 32.7%; NEt_3, 43.6%). The diaminate melted to a brown liquid in a 3° range at 75°C., and transformed slowly to the white and less dense tetraminate in liquid triethylamine at 20°C. The process of evaporation will affect the mole ratios in the tetrachloride–amine mixtures for, as judged by yields, conversion to the nonvolatile solids was by no means quantitative. The liquid condensates recovered while drying the silicon and germanium mixtures were yellow tinted solutions at − 78°C., but on warming towards 20°C. white suspensions again developed. The process was repetitive. In addition, oxygen gas had a definite effect on the silicon tetrachloride – amine mixtures, gas being absorbed with the simultaneous formation of a brown precipitate. Nitrogen gas had no effect on any of the preparations.

The behavior of the titanium tetrachloride – amine mixture in the vacuum preparation was in contrast to that of the group IV*b* elements. On warming from − 78°C. an intense red color spread in the amine as the frozen tetrachloride began to melt, but this disappeared abruptly when a quick spattering reaction produced a hard black solid. The latter substance had the approximate composition, $2TiCl_4 . NEt_3$ (Exp. Cl, 58.5%. Theor. Cl, 58.5%). However, its aqueous acid solutions were red and its basic precipitates blue to violet, color reactions usually associated with Ti(+ 3) rather than Ti(+ 4).

Solvent Preparations

The solvent used was 30–60 petrol ether, dehydrated with sodium wire; 100 ml. of 0.2 molal tetrachloride solution added at the rate of 2 ml. per min. were magnetically stirred into 300 ml. of 1 molal triethylamine solution at 20°C. in an atmosphere of dried nitrogen. The apparatus had previously been dried at 120°C. The products formed as thick white suspensions and precipitates, and, after being washed in petrol ether, were filtered with the aid of rubber dams and dried in vacuum. The experimental yields, based on the tetrachlorides, varied from 50% to 75% for silicon, and from 85% to 100% for germanium, tin, and titanium.

Silicon and titanium were measured as the dioxides after slow ignitions. Chlorine and triethylamine were determined volumetrically (9). Substantial ignition losses with germanium and tin compelled the use of a wet method for determining them. They were measured as the dioxides, recovered from the digestion of the corresponding tetraminates in concentrated nitric acid. Tin was also separately determined* by means of the organic reagent, N-benzoylphenylhydroxylamine, confirming and improving on the metastannate analyses. The

*Professor Ryan, Dalhousie University, who did the N-benzoylphenylhydroxylamine analyses, will publish the details of this method shortly.

analytical results are presented in Table II, calculated on the basis of the assumed formula in column 1. Experimentally, the compounds conform to the tetraminate

TABLE II
ANALYSES OF THE AMINATES

Compound	Analytical composition, moles/mole aminate		
	M*	Cl	NEt_3
$SiCl_4.4NEt_3$	0.99	3.89	3.94
$GeCl_4.4NEt_3$	0.95	3.90	3.92
$TiCl_4.4NEt_3$	0.93	3.76	4.12
$SnCl_4.4NEt_3$	0.99	4.14	4.00
$SnCl_4.3NEt_3$	1.00	3.88	2.90
$SnCl_4.2NEt_3$		4.08	1.96
$SnCl_4.NEt_3$		4.03	0.99
$2TiCl_4.NEt_3$		8.00	

*M is Si, Ge, Sn, or Ti.

representation agreeably enough except in the case of titanium, where the mole ratio of amine to tetrachloride is 4.5 rather than 4.

Two items in Table II require comment. The 'triaminate' of tin tetrachloride was a solvent preparation, but mixing occurred at 0°C., rather than 20°C. It was not possible to decide from the present work whether this was a real compound, or whether it was only a fortuitous combination of the di- and tetraminates. Another compound, the monaminate of tin tetrachloride, was prepared by adding triethylamine to excess tin tetrachloride. The product was a hard, dark, deliquescent solid, quite unlike the powdery di- and tetraminates.

Thermal Decomposition of the Tetraminates

The thermal decompositions were carried out in vacuum. Approximately 0.5000 gm. of the compounds were weighed out into a long tube that was then connected to a system containing a manometer and a trap. After thorough evacuation at room temperature the lower part of the tube, which contained the powder, was heated in an oil bath. All of the tetraminates developed vapor pressures of triethylamine on heating, and though these were not entirely independent of history and amount, the temperatures at which a vapor pressure of 20 mm. was created differentiated the tin tetraminate (ca. 65°C.) from the other three tetraminates (ca. 95°C.).

The amine was condensed into the trap at − 78°C. It was characterized by its vapor pressure, 20 mm. at 0°C., (7), and by analysis (back titrating a standard acid solution of the amine with a standard base, and then comparing the analytical weight with the gravimetric weight of the amine).

Another product, the hydrochloride of triethylamine, sublimed out of the decomposing reactant, and condensed as a solid on the walls of the cold part of the tube. The amine hydrochloride was characterized by determining the amine/Cl ratio, and by comparing analytic and gravimetric weights. Sodium fluorescein was the indicator in the titration for chloride with silver nitrate.

In preliminary runs it had been determined that the decomposition was a

process which occurred in successive stages. On first heating a vapor pressure developed. If the volatile products were removed at 100°C. until the vapor pressure of the partially decomposed solid was reduced to about 0 mm., a second product appeared. Triethylammonium chloride, a subliming solid with no measurable vapor pressure at room temperature, began to appear when the silicon, germanium, and titanium compounds were still dry white powders; but the tin tetraminate residue was a brown liquid with the composition of the diaminate. Only a limited amount of triethylamine hydrochloride could be extracted from the decompositions at 100°C. The next step in the decomposition did not occur until the temperature was in excess of 135°C. Then the products became more complicated. The hydrochloride fraction became weight deficient compared to Et_3N . HCl, a second component that was not an amine appeared in the volatile liquid product, and germanium and tin began to disappear from the decomposing residue.

The first two steps in the decompositions were then the evolution of triethylamine followed by the sublimation of the hydrochloride of triethylamine from the decomposing tetraminates. The yields of these two products, obtained at 100°C. in decompositions of one to two days duration, are listed for each of the four tetraminates in Table III. For each of the four compounds the sum of the two nitrogeneous products is almost equal to two moles of 'amine' per mole of tetraminate. That is, about one half of the amine contained in the tetraminate was removable at 100°C., and about one half was not. The form in which the amine appeared, however, whether as free amine or as the hydrochloride, varied considerably with the compound. For the compounds of silicon,* germanium, and titanium, the amine was preponderantly released in the form of the hydrochloride, although increasing amounts of triethylamine itself were recovered in the order silicon, germanium, titanium. Only in the decomposition of the tin tetraminate was triethylamine the major product. But when the tin tetraminate was decomposed at 150°C., the yield of triethylamine compared with the 100°C. decomposition was considerably reduced. It is to be noted that the amine hydrochloride recovered from the 150°C. decomposition had an experimental formula weight of 110 (column 5, Table III). The formula weight of triethylamine hydrochloride is 138.

TABLE III

THERMAL DECOMPOSITION OF THE TETRAMINATES

Tetraminate	Temp., °C.	Volatile products		
		Moles/mole tetraminate		Anal.g.F.W. NR_3.HCl
		Et_3N	NR_3.HCl	
$SiCl_4.4NEt_3$	100	0.1	1.8	138
$GeCl_4.4NEt_3$	100	0.4	1.8	137
$TiCl_4.4NEt_3$	115	0.8	1.5	
$SnCl_4.4NEt_3$	100	1.8	0.2	137
$SnCl_4.4NEt_3$	150	1.2	1.3	110

**The thermal decomposition of $SiCl_4.4Et_3N$ has been described before (9) but not in vacuum nor at constant temperature.*

DISCUSSION

Three rather different explanations can be offered for the aminates of the group IV tetrachlorides. First of all, they may be thought of as ionic compounds, of the type $M(NEt_3)_4^{+4},4Cl^-$. Of the IV*b* tetrahalides, tin tetrachloride, because of the low electronegativity of tin, would be the chloride most easily ionized. But it is just this element whose non-ionic addition compounds are best known. If the three reactions for which evidence has been given are considered

$$SnCl_4 + 2Et_3N = SnCl_4.2Et_3N,$$
$$SnCl_4 + 4Et_3N = SnCl_4.4Et_3N,$$
$$SnCl_4.4Et_3N = SnCl_4.2Et_3N + 2Et_3N$$
rev.

and it is recalled that a coordination number of six is well known for tin, the assumption of ionic compounds for the aminates of the group IV halides becomes difficult to defend.

On the other hand it may legitimately be considered, particularly in the case of $SiCl_4.4NEt_3$, that the tetraminates merely correspond to mixtures of the hydrochloride of triethylamine with some substituted tetra-covalent compound of the group IV element. To correspond with the experimental data, however, this would require a low temperature decomposition of the tertiary amine, quantitative substitution of only two chlorines in the tetrachloride, and complete insolubility of both the hydrochloride and the substituted covalent compound in petrol ether. It is not very likely that even one of these restrictions could be fulfilled.

A remaining alternative is that the aminates of the group IV halides be interpreted as molecular addition compounds. The thermal decompositions are then to be understood as a competitive situation involving two reactions; first of all, the simple molecular dissociation liberating triethylamine; and secondly, the internal degradations leading to the formation of the hydrochloride of triethylamine. The large yield of triethylamine from the tin tetraminate is to be associated with the relative stability of the tin diaminate, and with the comparative inertness of tin tetrachloride towards substitution reactions. The small yields of triethylamine from the tetraminates of silicon, germanium, and titanium may conversely be related to the increasing strengths in coordinate bonding, and to greater substitutive reactivity in the halides. In either case, successive stages in the decompositions would be expected. When very little hydrochloride is released by the tetraminate, the steps would correspond to the evolution of two moles of amine followed by the different reaction, the decomposition of the diaminate. While, in the other extreme, if only triethylamine hydrochloride is obtained at first, when two moles of it are removed necessarily different degradations in a substituted compound would follow. However, the situation is not sufficiently simple to conclude that the strengths of the bonds between amine and tetrachloride decrease in the order silicon, germanium, titanium, tin as the vapor pressures and the amine/hydrochloride ratio otherwise suggest. Still, it can be decided that the tetraminate of titanium may be considered along with the tetraminates of the group IV*b* elements, silicon, germanium, and tin. And

that the behaviors of these compounds are consistent with the assumption that they are molecular addition compounds.

To explain the molecular addition compounds of the group IV*b* tetrachlorides, it is necessary to assume that $n + 1$ type orbitals ((i.e., $(n + 1)s,nd$, $(n + 1)p$)) are functioning in the coordinate bonds that establish the compounds, whereas n type orbitals (i.e. ns, $(n - 1)d,np$) can be assigned to titanium tetrachloride. However, the proclivity of the two kinds of orbitals towards addition is not markedly different. That is, the electron structure of the group IV atom is not in itself decisive in establishing the stability of the vacant orbitals. If the orbitals are taken to be molecular, rather than atomic, then the contributions of the four chlorine atoms to the molecular orbitals, combined with the similar geometries of the molecules, will tend to make the different tetrachloride molecules more alike for purposes of addition. However, titanium is still not a regular member of the silicon, germanium, tin series, particularly in the distinctive compound $2TiCl_4 . NEt_3$.

The assumption of $n + 1$ type orbitals for the group IV*b* tetrachlorides may have some diagnostic value. For example, a consideration of the geometric and orbital factors in the group IV*b* tetrahalides leads to the conclusion that mono-, di-, tetra-, and hexaminates should be able to form as discrete addition compounds (8). Compounds corresponding to these four different ratios of amine to tetrachloride have been prepared. The mono-, di-, and tetraminates of tin tetrachloride with triethylamine have been reported above, and corresponding compounds between silicon tetrachloride and tertiary amines are known (8). In addition, the hexaminate of tin tetrachloride with ethylamine has been recently prepared (11).

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ADDITION COMPOUNDS OF THE GROUP IV HALIDES

II. ETHYLAMINE AND THE TETRACHLORIDES OF SILICON, GERMANIUM, TIN, AND TITANIUM[1]

By W. R. Trost

ABSTRACT

Aminates of tin tetrachloride and titanium tetrachloride are reported. On the bases of these compounds, and the recovery of a tetraminate, $SiCl_4.4EtNH_2$, from among the substitution products in the reaction of silicon tetrachloride with ethylamine at − 78°C., it is suggested that the transition state in the substitution reaction corresponds to an addition compound.

The reactions between ethylamine and the tetrachlorides of silicon, germanium, tin, and titanium have been studied in anhydrous ethyl ether as part of a program to discover evidence for addition compounds in the group IV tetrahalides (3). When 0.2 molal solutions of the tetrachlorides were magnetically stirred into 1 molal solutions of ethylamine at 0°C. in an atmosphere of nitrogen, the insoluble product was very largely $EtNH_3Cl$ (ca. 95%) in the case of the silicon and germanium tetrachlorides, but had the composition $SnCl_4.6EtNH_2$ (72% yield) and $TiCl_4.4EtNH_2$ (67% yield) in the case of the tin and titanium tetrachlorides respectively. The products were characterized analytically, and ethylammonium chloride was also identified by its melting point, 108°C. The analytical data for the tin and titanium aminates are shown in Table I, calculated on the basis of the formula in column 1, Table I. The preparative and analytical methods have been described in an earlier paper (3).

TABLE I

ANALYSES OF THE AMINATES

Compound	Analytical composition, moles/mole aminate		
	M*	Cl	$EtNH_2$
$SnCl_4.6EtNH_2$	1.00	4.02	6.1
$TiCl_4.4EtNH_2$	1.03	3.75	4.20
$SiCl_4.4EtNH_2$	0.99	3.85	4.15

*M is Si, Sn, Ti.

The tin and titanium aminates were partially decomposed, in vacuum, and the volatile products collected and analyzed (3). These data are given in Table II in terms of moles of product per mole of aminate. Only ethylamine volatilized from the tin aminate at 88°C. At the higher temperature, 140°C., both ethylamine and ethylammonium chloride appeared as products in the decomposition of the titanium aminate. Although the decomposition temperature was well above the melting point of ethylammonium chloride, the aminate remained 'dry' during the decomposition.

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Contribution from the Department of Chemistry, Dalhousie University, Halifax, N.S., with financial assistance from the National Research Council of Canada.

TABLE II

THERMAL DECOMPOSITION OF THE AMINATES

Aminate	Temp., °C.	Volatile products, moles/mole aminate	
		$EtNH_2$	$EtNH_2Cl$
$SnCl_4.6EtNH_2$	88	1.4	0
$TiCl_4.4EtNH_2$	140	0.7	1.3
$SiCl_4.4EtNH_2$	140	0.08	2.6

It is known that ethylamine can be made to react with silicon (1) and germanium tetrachlorides (2) to form silicon and germanium amides or imides that are soluble in ether, the balance of the reaction producing insoluble ethylammonium chloride. These reactions were assumed to have occurred when mixing took place at 0°C. In a second experiment, the temperature of the ethylamine solution was maintained at − 78°C. At the low temperature, the addition of 0.2 molal silicon tetrachloride produced a white suspension in the reaction mixture, together with a white crystalline precipitate that settled quickly when stirring ceased. By siphoning the suspension off the precipitate, and then removing the suspensoid by filtration, it was possible to separate three distinct components out of the reaction mixture. These were dried in vacuum and analyzed. The crystalline precipitate was ethylammonium chloride (Exp. Cl, 43.53; $EtNH_2$, 55.2; m.p. 109°C. Theor. Cl, 43.50; $EtNH_2$, 55.27; m.p. 108°C.). The substance remaining in solution in ether after the suspensoid had been removed contained silicon and amine, but had no chlorine. It was assumed to be $Si(NHEt)_4$ but was not identified. The third component, the suspensoid, had a composition approximately that of the tetraminate, $SiCl_4.4EtNH_2$, the analysis appearing in Table I. When heated in vacuum at 140°C., the compound did not melt although ethylammonium chloride was almost the only volatile product of the decomposition, as is shown in Table II. Under the same conditions, the ethylammonium chloride recovered in this preparation melted abruptly at about 110°C.

In view of these findings, together with the occurrence of addition compounds between tertiary amines and group IV tetrahalides (3), it is suggested that the transition state in the reactions of group IV tetrahalides with donor groups corresponds to a molecular addition compound that makes use of suitable $n + 1$ type orbitals in group IV*b* tetrahalides, and n type orbitals in group IV*a* tetrahalides.

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SYNTHESIS OF 2-METHYL-C^{14}-1,4-NAPHTHOQUINONE[1]

By R. V. Phillips,[2] L. W. Trevoy, L. B. Jaques, and J. W. T. Spinks

ABSTRACT

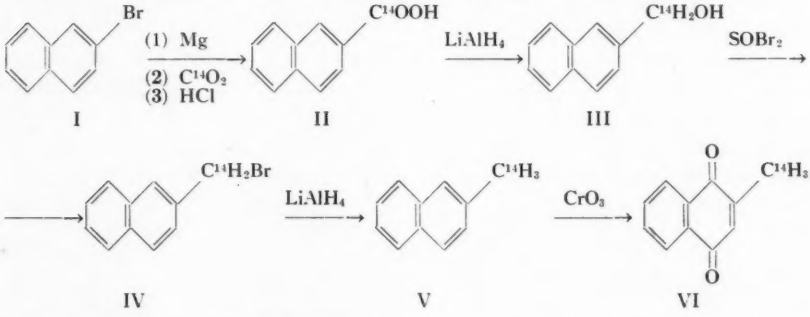
2-Methyl-1,4-naphthoquinone (menadione or vitamin K_3) has been synthesized labeled with C^{14} in the methyl group. Starting with 0.2 mc. of radioactive sodium carbonate, the intermediate compounds 2-naphthoic acid-carboxyl-C^{14}, 2-naphthalenemethanol-C^{14}, and 2-methyl-C^{14}-naphthalene were prepared. Oxidation of the latter compound by chromic oxide yielded 2-methyl-C^{14}-1,4-naphthoquinone with specific activity of 3.3×10^6 counts per min. per mgm. using a gas-flow type Geiger-Müller counter. Over-all yield was 23%.

INTRODUCTION

Tracer experiments involving the use of the anticoagulant dicumarol labeled with C^{14} have already been reported (7) and in this connection the antihemorrhagic compound 2-methyl-1,4-naphthoquinone (menadione) labeled with C^{14} was required.

The present communication reports a simple method for the preparation of 2-methyl-1,4-naphthoquinone from 2-bromonaphthalene and radioactive sodium carbonate. While this work was in progress two other preparative methods have been published, one by Collins (2) in which the C^{14} was incorporated in the C-8 position of the naphthalene ring, the other by Murray and Ronzio (8) in which methyl-C^{14} iodide was used to label the methyl group of menadione.

The first step in the synthesis involved the preparation (6) of 2-naphthoic acid-carboxyl-C^{14} (II) by carbonation with $C^{14}O_2$ of 2-naphthylmagnesium bromide. The acid was reduced by lithium aluminum hydride (9) to 2-naphthalenemethanol-C^{14} (III) and, after conversion to the corresponding bromide (IV), further reduction (11) yielded 2-methyl-C^{14}-naphthalene (V). Chromic acid oxidation of the hydrocarbon produced 2-methyl-C^{14}-1,4-naphthoquinone (VI). The over-all yield was 23% based on radioactive sodium carbonate.



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Contribution from the Departments of Chemistry and Physiology, University of Saskatchewan, Saskatoon, Sask. This paper constitutes a part of a thesis submitted by R. V. Phillips in partial fulfillment of the requirements for the Master of Arts degree.
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A better yield of 2-methylnaphthalene was obtained in preliminary experiments when the intermediate naphthalenemethyl bromide was not isolated but was reduced directly to the hydrocarbon. This procedure, therefore, was followed in the synthesis of radioactive 2-methyl-1,4-naphthoquinone.

EXPERIMENTAL

2-Naphthoic Acid-carboxyl-C^{14}(II)

Apparatus used for carbonation of the Grignard reagent was similar to that described by Collins (3).

A solution of 2-naphthylmagnesium bromide was prepared under nitrogen from 0.30 gm. of magnesium turnings and 1.55 gm. of 2-bromonaphthalene. The reaction was started in ether and then the solvent mixture consisting of benzene (one volume) and ether (three volumes) was added to bring the volume to 15 ml. The reaction mixture was refluxed for one hour and was diluted with the same solvent mixture to 25 ml. The concentration (5) of the solution was found to be 0.28 *M*.

Carbon dioxide generated by the addition of 8 ml. of 5*M* perchloric acid to 0.335 gm. (2.70 mM., 0.2 mc.) of sodium carbonate reacted with 3.3 mM. of 2-naphthylmagnesium bromide at − 25°C. Unreacted carbon dioxide was collected in a barium hydroxide trap. After hydrolysis with cold 4*N* hydrochloric acid the ether layer was separated and was extracted with 10% sodium hydroxide using an extractor of the type described by Collins (3). Acidification of the alkaline solution, extraction with ether, followed by evaporation of the ether, yielded the crude 2-naphthoic acid-carboxyl-C^{14}. After recrystallization from toluene the acid weighed 0.328 gm., m.p. 180–181°C. (lit. (2) m.p. 181–183.5°C.); yield 70%. (The yield is 80–85% based on recovered $C^{14}O_2$.)

2-Naphthalenemethanol-C^{14}(III)

2-Naphthoic acid-carboxyl-C^{14}(II)(0.230 gm.) was reduced to the corresponding alcohol by 1.4 mM. of lithium aluminum hydride in ether solution. The colorless product was recrystallized from benzene – petroleum ether to yield 0.183 gm. (97%) of 2-naphthalenemethanol-C^{14} m.p. 79–79.5°C. (lit.(1) m.p. 80°C.).

2-Methyl-C^{14}-naphthalene

2-Naphthalenemethanol-C^{14} (0.182 gm.) dissolved in 5 ml. of ether was cooled to − 80°C. and mixed with 0.27 gm. thionyl bromide. The reaction mixture stood at room temperature for one and one-half hours and then was added to an ethereal solution of 4.0 mM. of lithium aluminum hydride. 2-Methyl-C^{14}-naphthalene recovered from the ether solution was purified by sublimation at 20 mm. pressure and 50–80°C. The yield was 0.123 gm. (71%) melting at 33.5–34°C. (lit.(10) m.p. 34.6°C.).

2-Methyl-C^{14}-1,4-naphthoquinone

A solution of chromic anhydride was prepared by dissolving 7 gm. of the anhydride in a mixture of 7 ml. water, 4.2 ml. glacial acetic acid, and 0.66 ml. concentrated sulphuric acid. A solution of 0.107 gm. 2-methyl-C^{14}-naphthalene in 1 ml. glacial acetic acid mixed with 0.75 ml. of the chromic oxide solution was

shaken for five minutes at 50°C. Addition of 4 ml. water caused the solution to deposit the crystalline quinone. After being washed several times with water the 2-methyl-C^{14}-1,4-naphthoquinone was recrystallized from methanol to yield 0.0516 gm. (40–42%) of quinone, m.p. 103.5–104.5°C. (lit.(4) m.p. 105–106°C.). Radioactive measurements using a gas-flow type Geiger-Müller counter with a scale of 64 indicated a specific activity of 3.3×10^5 counts per min. per mgm. for an infinitely thin sample.

ACKNOWLEDGMENTS

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DENSITY DISTRIBUTIONS IN A VERTICAL TUBE CONTAINING XENON NEAR THE CRITICAL TEMPERATURE AS MEASURED BY A RADIOACTIVE TRACER TECHNIQUE[1]

By M. A. Weinberger[2] and W. G. Schneider

ABSTRACT

The variation of density with height has been determined for xenon confined in a long vertical bomb under near critical conditions. The densities were deduced by means of radioactive tracer techniques. Radioactive Xe^{127} was added to ordinary xenon and counting rates (assumed proportional to local densities) were measured at various positions along the bomb. The observed density distributions can be entirely explained by the influence of gravity on the system; a comparison of the observed density distribution with that calculated using the measured PV isotherms for xenon shows satisfactory agreement.

INTRODUCTION

In a recent paper (11) the authors showed that the shape of the liquid–vapor coexistence curve near T_c depended markedly on the vertical height of the containing bomb. This was explained in terms of large density gradients set up by the gravitational field. This behavior is a direct consequence of the S-shaped nature of the PV isotherms as well as the high compressibility of the system. In order to observe the density distribution in a system near the critical point more directly, the experiments described in the present report were undertaken. The measurements were made with xenon, which, because of its high molecular weight, may be expected to exhibit somewhat exaggerated density gradients in the region of the critical temperature. A tracer technique was employed. This involved the addition of the radioactive isotope, Xe^{127} (half life $\backsim$ 34 days), the assumption being made that the concentration of the tracer activity at any point in a long vertical tube is a measure of the local density. The distribution in density as a function of height in the tube was then easily obtained by moving an external counter along the tube.

The results obtained by the present methods confirm, in many respects, the measurements of Maass and co-workers (6) using a quartz spiral density balance, especially as regards the persistence of a density gradient above T_c. In the latter measurements, however, large hysteresis effects were always observed, and the question arose whether stirring or agitation had been sufficient to hasten equilibrium and whether the density gradients measured were really equilibrium properties of the system. For this reason it was decided in the present experiments to carry out measurements only after the system, thermostated at a given temperature, had been vigorously stirred and then allowed to stand for varying intervals of time. Vigorous stirring such as has been employed in this work, as well as in previous measurements in the region of the critical temperature (2, 3,

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8, 11), was found to be extremely effective, as evidenced by the excellent reproducibility in the measurements both on heating and cooling.

It was also hoped by the present methods to investigate the possibility of large molecular clusters settling out at the bottom of the tube at temperatures slightly above but very near the critical temperature. Density gradients due to the gravitational field may be expected to be set up very rapidly after the system has been vigorously stirred, while if sedimentation occurs, additional density gradients should appear after the system has been allowed to stand for some time. An apparent settling out in the present sense may also arise as a result of the greater compression at the bottom of the tube due solely to the gravitational gradient; the latter would be expected to favor the growth of large molecular clusters at the bottom end of a vertical tube, and "solution" of clusters at the upper end.

EXPERIMENTAL

Preparation and Purification of Xe^{127}

The xenon-127 was produced by Dr. P. H. Abelson, Carnegie Institution, Washington, by cyclotron bombardment. The nuclear reaction involved is $I^{127} + d \rightarrow Xe^{127} + 2n$ (9). The target was prepared by coating a copper grid with sodium iodide. After exposure, the copper grid was placed in an airtight glass container equipped with a breakable seal. The radioxenon was occluded in the sodium iodide and was liberated by dissolving the target in water.

The use of sodium iodide as target caused some difficulties (1). When the irradiated material was exposed to air on removal from the cyclotron, moisture was rapidly absorbed, leading to loss of radioxenon. An attempt to use the nonhygroscopic potassium iodide was unsuccessful. However, by cutting down the time of exposure to air, the absorption of moisture by the sodium iodide target was minimized and there was then no obvious deliquescence of the material.

The target container was attached to a vacuum system and the seal broken by a magnetically operated pin. After some ordinary xenon was added as carrier gas, the air in the container was removed with a Toepler pump, the air being passed repeatedly through traps cooled with acetone – carbon dioxide and with liquid nitrogen, respectively. A total of about 130 pumping operations were carried out before the apparatus was evacuated finally by means of a conventional high vacuum system. It was noticed that radioactive material had already been frozen in the liquid nitrogen trap at this stage.

Water saturated with xenon was then run into the container and a further batch of carrier xenon added. The water, which disintegrated the target material, was finally boiled to expel the xenon. The latter distilled into the liquid nitrogen cooled trap. The water which had condensed in the acetone – carbon dioxide cooled trap was boiled and refrozen and any liberated xenon condensed in the liquid nitrogen trap which was then shut off from the container system.

The condensed xenon was warmed in an acetone – carbon dioxide bath and distilled over phosphorus pentoxide into a liquid nitrogen cooled vessel. This

distillation was repeated and finally the xenon was distilled directly from acetone – carbon dioxide into the storage trap.

The method of filling the observation bomb was essentially the same as that used in previous experiments (11).

The Apparatus

A diagram of the apparatus is shown in Fig. 1. The observation bomb *A*,

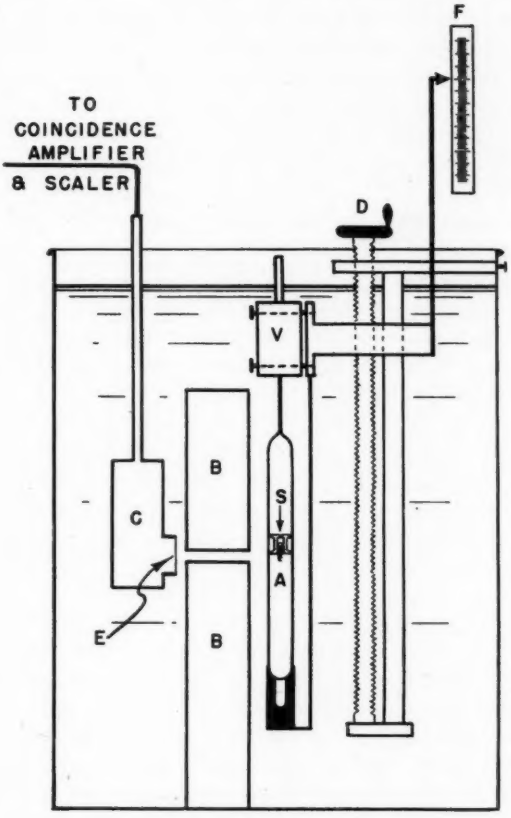

FIG. 1. Diagram of apparatus.

19 cm. long, was attached by a Kovar seal to the fittings of the high pressure valve *V* fixed to a platform which could be moved vertically by means of a threaded shaft *D*. The bomb was equipped with an internal stirrer slug *S* moved magnetically as described previously (11).

The lead shield and collimator *B* was $\frac{3}{4}$ in. thick and had a slit of $\frac{3}{8}$ in. width. Its distance from the bomb was $\frac{1}{4}$ in., whilst the copper foil window of the counter *C* pressed against the other side of the slit. The scintillation counter *C* consisted

of an anthracene crystal 1 in. × 1 in. × ¼ in. Scintillations were "seen" simultaneously by two selected No. 931A photomultiplier tubes housed behind the crystal. The whole assembly was mounted in a waterproof and lightproof brass case, a thin copper foil *E* being soldered to the case in front of the crystal.

The output from the photomultiplier tubes was fed into linear amplifier circuits and finally combined to trigger a circuit biased so that only coincident pulses were recorded. The amplified pulse was then applied to a Berkeley Scaler Model 1000B, through a 0.001μf. condenser to eliminate the d-c. voltage from the scaler.

The remainder of the apparatus was the same as that described previously (11). A point worth mentioning here was the use of d-c. for the intermittent heating of the bath for temperature control. It was found that a-c. heaters interfered with the counting circuits. This was especially noticeable with a thyratron circuit used in earlier experiments for proportional control of the intermittent heating.

A pointer was attached to the moving bomb assembly and indicated on a scale *F* the relative positions of bomb and collimator slit.

Procedure

As it was not thought advisable to disturb the observation bomb once it had been filled with the radioxenon, the steadiness of the counter and amplifier could not be tested during the run which extended over the period of a week. The method adopted was to count the radiation from a Co^{60} source placed against the collimator slit before and after the run.

After the amplifier was adjusted and the counting rate of the Co^{60} source taken, the observation bomb was filled with the radioxenon – ordinary xenon mixture to a density as close as possible to the critical density 1.105 gm. per cc. using the method previously described (11). The actual density was found to be 1.110 gm. per cc. The bomb was then carefully aligned with the collimator, the thermostat filled and warmed up to the required temperature.

When temperature equilibrium had been reached, counts were taken with various parts of the bomb opposite the collimator slit. The positions of the bomb were read on the scale. Counting periods were of five minute duration and at least three counts were made for each position. The temperature of the bath was observed during the counting, using a platinum resistance thermometer.

Temperature variation did not exceed ± 0.0005°C. during counting periods and ± 0.001°C. during the time taken for counting at a dozen positions of the bomb.

At the end of the run the xenon was condensed back into the brass weighing bomb and the background count measured, followed by the redetermination of the counting rate of the Co^{60} source.

RESULTS AND DISCUSSION

Treatment of Data

It was found that the counting rate for a given bomb position at a given temperature decreased with time much more rapidly than would be expected for an isotope with a half life of 34 days.

Half life times were calculated from three pairs of curves and are shown in Table I. The background count of 60 counts per min. was subtracted from all

TABLE I

Temperature, °C.		Counts per minute	Time interval, hr.	Half life, days
17.550		812	46	8.75
17.552		706		
15.619	vapor	694	147	9.3
15.624	vapor	462		
15.619	liquid	980	146	9.3
15.624	liquid	645		
17.550		812	88.5	8.7
16.730		640		
				Av. 9 ± 0.3

counting rates shown in the table. As can be seen, the actual half life time of the radioxenon is only approximately nine days. Another method utilizing all the curves was to read the counting rate, c, corresponding to the center of the bomb, from the various curves and to plot the value of $\log(c - 60)$ vs. time applicable to the reading. This plot, shown in Fig. 2, is a straight line with a fair

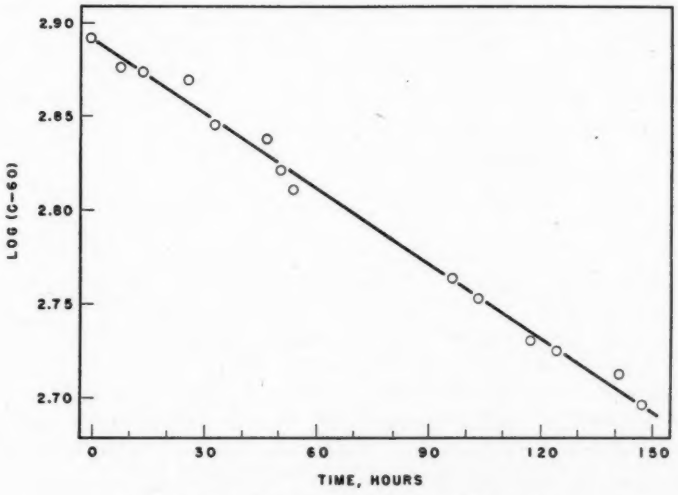

FIG. 2. Decay of tracer: Plot of log $(c-60)$ vs. time.

amount of scatter, having a slope equivalent to a half life of 224 hr. and this value was used for correcting the curves for decay.

Thus the half life of the xenon used in this work was about nine days. This value is close to the half life time of 8.0 ± 0.2 days found for the radioactive isotope Xe^{129} recently discovered by Bergström (4). It is, however, very doubtful that the present isotope was Xe^{129} as that would mean a (d,γ) reaction for its formation:

$$I^{127} + d \rightarrow Xe^{129} + \gamma.$$

Energetic and cross-section considerations (1) do not favor such a reaction. On the other hand from the method of preparation and purification employed the active substance must have been some isotope of xenon.

The counting rates corrected for decay and background for various positions of the bomb relative to the slit and for various temperatures are shown in Figs. 4, 5, and 6. The two dashed vertical lines in the figures indicate the geometrical resolution of the slit with respect to the meniscus. They correspond to the bomb positions shown in Fig. 3 and enclose a region where radiation from the meniscus could reach the counter if the screening by the lead were perfect.

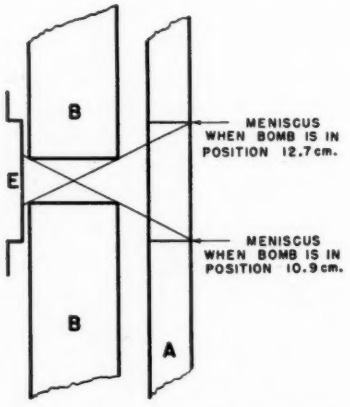

FIG. 3. Geometry of counter and bomb arrangement.

Fig. 4 shows the type of behavior over a temperature range ± 1°C. around the critical temperature. Of especial interest at this stage is curve *i* which was taken at 0.966°C. below the critical temperature 16.590°C. Here there are comparatively large density differences between liquid and vapor, and there is no opalescence so that the meniscus is very sharply defined. Counts in bomb positions below 10.9 cm. therefore correspond to vapor and those in positions above 12.7 cm. to liquid if the resolution is perfect. In between, the counting rate rises as more and more liquid comes across the slit. The effectiveness of the screening by the lead shield can be gauged by comparing the ratio of the counting rate in position, say, 0.2 cm. below 10.9 cm. to that in position 0.2 cm. above

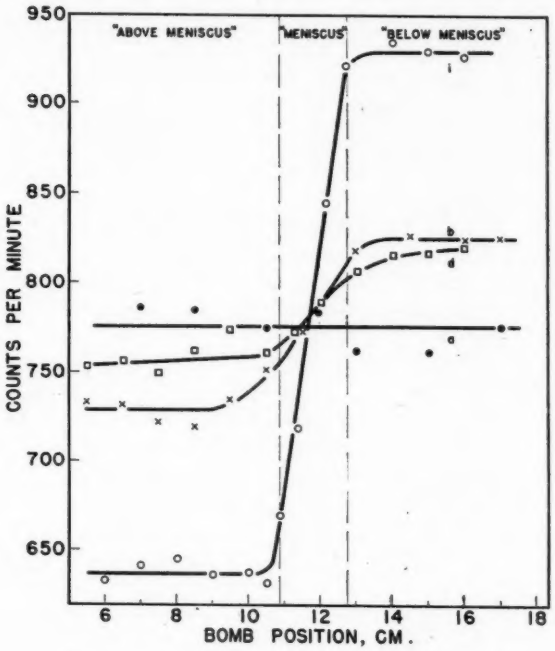

FIG. 4. Tracer activity for various bomb positions.
○ Curve i : measured at $T_c - 0.966°C.$
× Curve b : measured at $T_c + 0.013°C.$
□ Curve d : measured at $T_c + 0.061°C.$
● Curve a : measured at $T_c + 0.960°C.$

12.7 cm. with the ratio of vapor to liquid density at 15.624°C. obtained from the coexistence curve of xenon (11). The counting rate ratio is 643/925 = 0.696 and the density ratio $0.840/1.377_5 = 0.610$. Thus the contribution to the counts of a 2.2 cm. bomb portion from the remainder of the bomb is of the order 20–30%. The resolution was thus not too good but little could be done about it as the activity of the xenon was not sufficiently high to allow improvement of the collimation.

Curve a, Fig. 4, was taken immediately after stirring at 17.550°C., i.e. 0.96°C. above the critical temperature. No opalescence was present in the system and within the scatter of the experimental points no density gradient is apparent at this temperature.

Curve b at 0.013°C. above T_c shows a marked density gradient. Here the system was allowed to stand for one hour before counting was started. A ring of heavy opalescence was present at the center of the tube. The density gradient is still present at 0.061°C. above T_c, curve d, Figs. 4 and 5, where a light opalescent band was present in the middle region of the bomb.

Other curves taken at temperatures in the more immediate neighborhood of

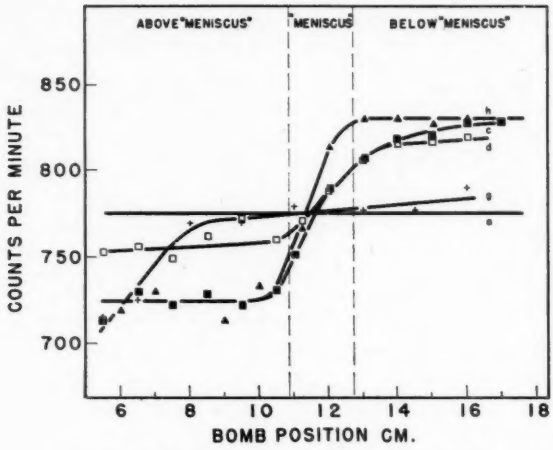

FIG. 5. Tracer activity for various bomb positions.
▲ Curve *h* : measured at $T_c + 0.003°C.$
■ Curve *c* : measured at $T_c + 0.029°C.$
□ Curve *d* : measured at $T_c + 0.061°C.$
\+ Curve *g* : measured at $T_c + 0.140°C.$
Curve *a* : measured at $T_c + 0.960°C.$ Points not shown.

T_c are shown in Fig. 5. Curve *h* was taken at 0.003° above T_c, curve *c* at 0.029°C. above T_c, curve *d* at 0.061°C. above T_c, and curve *g* at 0.14°C. above T_c. The position of curve *a* is indicated for comparison purposes.

The information relevant to curves in Figs. 4, 5, and 6 is summarized in Table II.

TABLE II

Curve	Temperature, $T_c \pm x$°C.	Time of commencement of counting after stirring	Time taken for whole curve, hr.	Opalescence
i	− 0.966	15 min.	$3\frac{1}{2}$	None
h	+ 0.003	$17\frac{1}{2}$ hr.	3	Narrow band
b	+ 0.013	1 hr.	$3\frac{1}{2}$	Opalescence in middle of tube
c	+ 0.029	$3\frac{1}{2}$ hr.	4	Opalescence in middle of tube, "homogeneous" at start
d	+ 0.061	3 hr.	4	Opalescence in middle of tube
e	+ 0.140	Immediately	1	"Homogeneous". Pale opalescence did not "concentrate" during the run period
f	+ 0.140	$6\frac{1}{2}$ hr.	$2\frac{1}{2}$	
g	+ 0.140	$20\frac{1}{2}$ hr.	$2\frac{3}{4}$	
a	+ 0.960	Immediately	$3\frac{1}{4}$	None

The chronological order of the curves was as indicated by their alphabetical order.

The Effect of Time on the Density Gradient

At those temperatures where a medium to heavy opalescence was present the visible effect of time was a "concentration" of the opalescence towards the middle of the bomb. At those temperatures counts were usually taken after the opalescence region had shrunk in this way. Thus curve *h* (Fig. 5) was taken $17\frac{1}{2}$ hr.

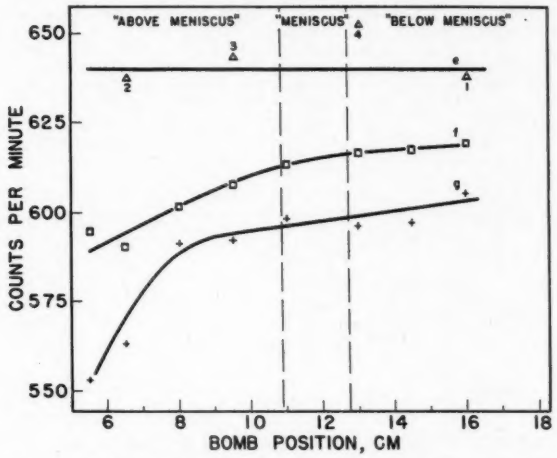

FIG. 6. The effect of time on density gradient at $T_c + 0.140$°C.
△ Curve *e* : measured immediately.
□ Curve *f* : measured after 6½ hr. standing.
+ Curve *g* : measured after 21 hr. standing.

after stirring when the opalescent band was only ∽ 3 mm. wide. In this case, however, counts were also observed 30 min. after stirring when the opalescence was still fairly well distributed throughout the bomb. The resulting curve (not shown) was the same as curve *h* within experimental error. This would indicate that the density gradients are established fairly rapidly when they are moderately large and that they have no direct relation to the visible distribution of opalescence.

In a further series of measurements to study the effect of time on the density gradient, the temperature was chosen at 0.140°C. above T_c. Throughout the whole of the run there was a very pale straw colored opalescence distributed throughout the tube and this opalescence did not "concentrate" during the period of the run. The curves are shown in Fig. 6. They are not corrected for decay in order to avoid overlapping of the curves. Curve *e* was taken immediately after stirring, the order of the counts at each height being indicated by numerals under the points, each point requiring 17 min. The trend of the points would indicate a variation of the density distribution during the counting period and perhaps a straight line should not be drawn through the points. Curves *f* and *g* give the density distribution observed respectively 6½ hr. and 21 hr. after the measurement of curve *e*. Thus there seems to be some change with time. However, until the resolution of the method is improved and more precise data become available it is best to reserve judgment on this point.

Comparison of Density Gradient with that Calculated from Isotherms

Densities at various heights of the bomb were calculated using the isotherms of xenon measured in this laboratory by Dr. H. W. Habgood (5). The calculation was done graphically using the method described previously (11). The results

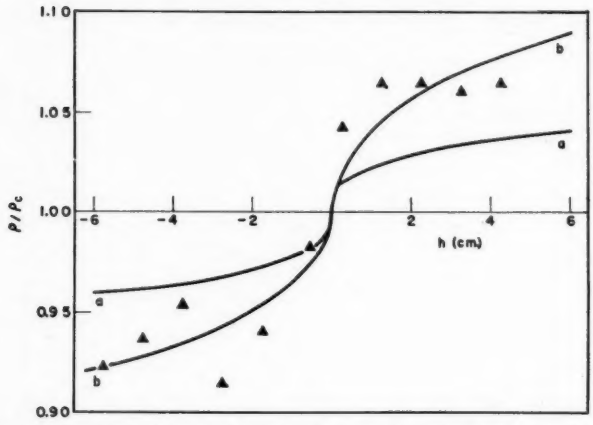

FIG. 7. Plot of density relative to critical density at various heights below (+) and above (−) meniscus position.
(*a*) Relative density distribution calculated from van der Waal's critical isotherm.
(*b*) Relative density distribution calculated from Habgood's isotherm at 16.590°C.
Points are ratios of counting rates at various positions to that at the "meniscus" level. Measured at 16.593°C.

are shown in Figs. 7, 8, and 9 in terms of the density relative to the critical density at various heights h below (+) and above (−) the positions where the meniscus disappeared at the critical temperature. In Fig. 7 the curves shown are (*a*) the density distribution calculated on the basis of the van der Waal's critical isotherm at 16.590°C. as used previously (11) and (*b*) the density distribution derived from Habgood's isotherm at 16.590°C. The points indicate the ratio of the counting rates at various positions to that at the "meniscus" level in the tube. These

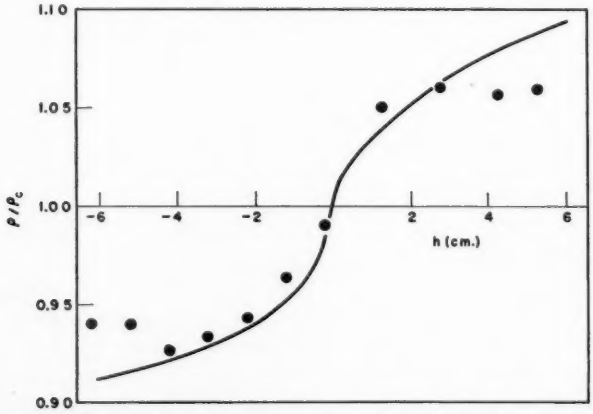

FIG. 8. Plot of relative density at various heights below (+) and above (−) original meniscus position calculated from Habgood's isotherm at 16.600°C. Points are count ratios at 16.603°C.

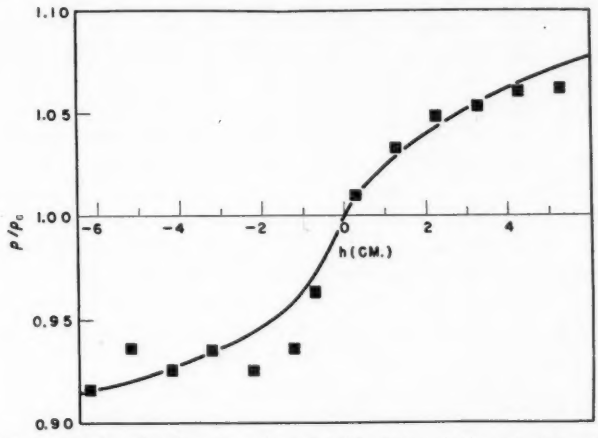

FIG. 9. Plot of relative density at various heights below (+) and above (−) original meniscus position calculated from Habgood's isotherm at 16.620°C. Points are count ratios at 16.619°C.

counts were made at 16.593°C. (T_c+ 0.003°C.). Fig. 8 shows the density distributions derived from Habgood's isotherm at 16.600°C. and the points represent count ratios at 16.603°C. Fig. 9 gives the data at an isotherm temperature of 16.620°C.; the counts were made at 16.619°C.

As found previously (11) the density distribution calculated on the basis of the critical van der Waal's isotherm only accounts for a part of the actual density variation found. However, when the measured xenon isotherms are used, the observed variation in density is, within the limits of experimental error, completely accounted for by gravitational effects. It is doubtful whether redetermination of the density distribution using better collimation would materially affect this conclusion. In the present results, all counting rates are too high owing to contributions from supposedly screened parts of the bomb. More precise collimation would have lowered the general level of the counts but would not appreciably affect the shape of the counting rate – bomb position curve.*

Thus these experiments confirm the great importance which must be attached to the influence of gravity on the density distribution in systems near the critical temperature. It would also seem that molecular clustering plays a minor part in determining the actual density distribution. There is no evidence from these experiments in support of the idea that molecular clusters sediment according to their size and thus set up an additional density gradient.

While the present results largely confirm the phenomena observed by Tapp, Steacie, and Maass (10) and Winkler and Maass (12) with methyl ether regarding the persistence of a density gradient of temperatures above T_c, there are a

* *The leveling off of the points at either side in Figs. 7, 8, and 9 is probably due to end effects. This is especially noticeable on the higher density side and is explained by the fact that at* $h \approx 6$ *cm. the stirrer slug resting at the bottom comes into the geometrical resolution range of the counter. Imperfect collimation would account for the effect being noticed at smaller heights.*

few discrepancies. The range of temperatures above T_c at which the density gradient persists is much smaller in the case of xenon than in the case of methyl ether (less than 1°C. as against ∽ 10°C.). Correspondingly, density gradients of comparable magnitude exist for xenon at 0.02°C. above T_c and for methyl ether at 0.2°C. above T_c. In the case of xenon we have seen that the density gradients can be satisfactorily accounted for by assuming the influence of the gravitational effect alone. Isotherms are not available to calculate the gravitational effect for methyl ether, but it does seem doubtful that it alone can provide the explanation in this case. Again in the case of ethylene Maass and Geddes (7) estimated the gravitational effect to account for only a small fraction of the actual density gradient observed. It is quite possible that the stirring method used by Maass and co-workers was not too efficient. For example, in all the above mentioned papers it was stressed that density differences, which were unaffected by "stirring", did not reappear once they had been destroyed by heating, and only reappeared on cooling, at a much lower temperature, with formation of the liquid phase. In the present work with xenon such behavior was not found; density gradients reappeared quite reproducibly (cf. curve *b* and curve *a*, Fig. 4. Curve *b* was taken after cooling the system from 0.96°C. at which there was no gradient to 0.013°C. above T_c, stirring continuously). The hysteresis in the systems studied by Maass points to the existence of metastable states undisturbed by inefficient stirring.

Finally it should be pointed out that, owing to insufficient activity of the radioactive tracer Xe^{127}, it was not possible to approach the accuracy in the density measurements achieved by Maass and co-workers with the quartz spiral balance. With a higher tracer activity and better collimation, the accuracy of the present measurements could be improved. Although this may be expected to alter the shape of the density vs. height curve slightly (particularly in the region of the "meniscus" level), the over-all density gradient (assuming the containing tube to be of sufficient length) will be essentially the same. It is believed, therefore, that greater precision in the density measurements will not alter the present conclusions regarding the density gradient and its dependence on the gravitational field.

ACKNOWLEDGMENTS

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THE ACTION OF HYDROXYLAMINE, ITS *o*-METHYL ETHER, AND THEIR HYDROCHLORIDES ON CELLULOSE TRINITRATE IN PYRIDINE[1]

By G. H. Segall[2] and C. B. Purves

ABSTRACT

Solution of cellulose trinitrate in dry pyridine containing an excess of hydroxylamine base caused the evolution of 1 mole of nitrogen gas of 99% purity and the formation in high yield of a fibrous cellulose substituted with 1.7 nitrate and about 0.08 oxime groups per glucose unit. The replacement of the hydroxylamine by *o*-methylhydroxylamine suppressed the evolution of gas in the above reaction but the product was similar except for a small substitution (about 0.2) of methyloxime groups. Replacement of hydroxylamine base by the hydrochloride altered the composition of the evolved gas to nitrous oxide, about 85%, and nitrogen, about 15%. The fibrous product, isolated in high yield, had the composition of a cellulose substituted with 1.7 nitrate and about 1 oxime groups. No gas was produced in the parallel experiments with *o*-methylhydroxylamine hydrochloride and the product contained 1 methyloxime instead of 1 oxime unit.

The above partial denitrations involved only an incidental degradation of the cellulose trinitrate, and probably only nitrate groups in the second, or third, rather than the sixth, positions of the glucose residues. All four products had a wide solubility in organic liquids and were remarkable for their relatively great stability toward pyridine or caustic soda.

INTRODUCTION

Previous researches, which were adequately reviewed elsewhere (19, 30), showed that alkali rapidly changed nitrocelluloses to a less highly nitrated, oxidized condition (14, 23), and eventually to small molecules such as oxypropionic acid (6). According to Kenyon and Gray (19), 60 to 70% of the nitrate groups removed by aqueous caustic soda could be recovered as sodium nitrite, and the other products included reducing substances as well as carbon dioxide. It was therefore likely that alkali caused the elimination of at least some of the nitrate groups in nitrocellulose by the redox route, $R_1R_2CHONO_2 \rightarrow R_1R_2C = O + HNO_2$, simpler cases of which were recently discussed (4). The excess alkali would then rapidly degrade the partly nitrated, reducing oxycellulose so formed (11). Although dry pyridine at room temperature usually has little action upon carbonyl groups, Angeli (1) found that by solution in pyridine a cellulose nitrate not only lost about one-third of its nitrate groups but was degraded to an amorphous powder. Danilov and Mirlas (10), indeed, decided that the reduction in the viscosity of nitrocellulose solution caused by pyridine was greater than that brought about by the strong bases sodium hydroxide and tetramethyl ammonium hydroxide. The present research arose from a repetition of Angeli's curious observation, and from attempts to include with the pyridine a reagent capable of condensing with any carbonyl groups formed, and of protecting them from further change. General considerations also suggested that nitrate groups would be removed from the second, third, and sixth positions at different rates,

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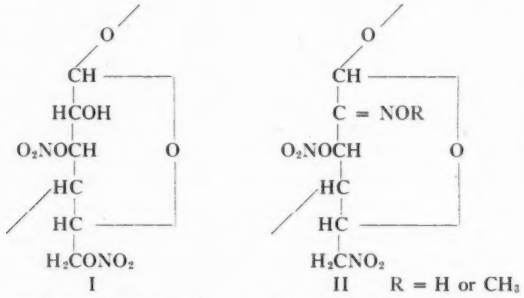
and perhaps even in a selective way, but technical difficulties prevented a full investigation of this possibility.

When 1 gm. of cellulose trinitrate was dissolved in 25 cc. of pure dry pyridine at room temperature, the viscosity of the solution, originally high, diminished to that of the solvent within two days; the solution became deep yellow or orange, and the addition of much water precipitated a 40% yield of cellulose with a nitrogen content of 12.0% (substitution 2.2). The yield was only 15% when five days elapsed before the addition of the water. When, however, the original pyridine solution contained a large excess, 5 gm., of pure hydroxylamine, practically no color developed, the viscosity decreased much more slowly although the reaction was still exothermic, and large volumes of a colorless gas were vigorously evolved. This gas was shown by analysis in an Orsat apparatus and by its density to be nitrogen of 99% purity, and in one experiment the moles collected per glucose residue in the trinitrate were 0.94 and 1.05 after 4.5 and 11 hr., respectively. A second experiment yielded 1.00 moles in 13 hr., and thereafter the gas evolution was exceedingly slow. These values were correct, in spite of the fact that the formation of gas in similar experiments with many technical nitrates was much greater (16). Precipitation of the solution after 11 hr. gave a nearly quantitative yield of strong white fibers whose total nitrogen content of 10.6% corresponded to a substitution of 1.9. A lower nitrate nitrogen content of 10.0%, however, suggested a substitution of 1.70 nitrate and 0.08 oxime groups. These substitutions remained practically unchanged at 1.68 and 0.08, respectively, when the reaction was allowed to proceed for 76 hr., although in this case the viscosity of the original solution was considerably lower. In agreement with this observation, the nitrogen content of the fibers was not changed by re-solution for three days in pyridine–hydroxylamine, and decreased by only 0.4% after solution for 18 hr. in pure pyridine.

Several attempts to detect the carbonyl groups expected in the fibers by condensation with *o*-methylhydroxylamine, CH_3ONH_2, introduced only 1% or less of methoxyl groups (substitution 0.08 or less) and the reaction was presumably restricted to the replacement of the oxime already present by *o*-methyloxime units. Attempts to remove the supposed oxime group by hydrolysis with 0.5% sulphuric or 1.5% hydrochloric acid in various solvent mixtures at room temperature for several days gave negative results, but methylation with diazomethane introduced 0.5% of methoxy groups (substitution 0.04). These groups probably corresponded to the *o*-methyloxime because diazomethane, when anhydrous, was known not to methylate aliphatic alcohols of an ordinary type. Although free carbonyl groups could not be detected in the fibers, the presence of free hydroxyl groups was readily demonstrated by renitration with the nondegrading nitric acid – phosphorus pentoxide mixture recommended by Berl (5), and by acetylation to a soluble, fibrous acetate whose nitrogen content corresponded to an additional substitution of 1.0 acetyl groups. Replacement of the nitrate with acetyl groups by "reductive acetylation" (17) with zinc dust, acetic anhydride, and trimethylamine was unsatisfactory and resulted in a brown powder with an acetyl substitution of only 2.5. Ice-cold ammonium hydrosulphide, however,

gave a 98% yield of a crude, fibrous cellulose that could be renitrated to the trinitrate level. The action of hydroxylamine in pyridine on the original cellulose nitrate, of substitution about 2.9, was therefore to replace about 1.2 nitrate groups with 0.08 oxime and about 1.0 hydroxyl groups, and so form a cellulose "dinitrate" (Structure I).



Positions of nitrate groups arbitrary, but identical in I and II.

This "dinitrate" was remarkable not only in being soluble in an unusually wide range of organic liquids, but also in its relatively great stability toward alkali. It could, for example, be methylated in 80 to 85% yield with dimethyl sulphate and 30% sodium hydroxide to soluble, brittle white fibers with unchanged nitrate and oxime substitutions, but with an additional methoxyl substitution of about 0.9. Unfortunately, conditions were not found in which the denitration of this "cellulose dinitrate monomethyl ether" could be satisfactorily accomplished with ammonium hydrosulphide, and the substance was recovered unchanged from an attempted hydrogenation over a palladium – calcium carbonate catalyst. The claim that this catalyst reduced sugar nitrates rapidly and nearly quantitatively to the parent compounds (20) was confirmed. Failure to prepare the methylcellulose in an adequate state made it necessary to postpone attempts to locate the distribution of the methyl groups among the second, third, and sixth positions of the glucose residues in the cellulose (24), and thus to determine the positions occupied by the nitrate groups in the "dinitrate". Some of these groups were probably present in the sixth position, because the "dinitrate", when heated with excess sodium iodide in acetone, gave an 89% yield of a gray-brown powder analyzing for substitutions of 0.8 for iodine and 0.5 for nitrate. Work with nitrated glucose derivatives discussed elsewhere (28, 29) made it likely that in this reaction nitrate groups substituted in the sixth or primary alcohol positions would be replaced by iodine, whereas those in secondary alcohol positions might be removed but would not be replaced. An attempt to determine the unsubstituted 2,3-glycol groups in the crude methyl cellulose by oxidation with periodic acid (25) gave untrustworthy results.

The substitution of hydroxylamine hydrochloride for the free base present in the cellulose trinitrate – pyridine solution just discussed also prevented a rapid decrease in viscosity and the development of color. The gas evolved, however,

proved to be 85% nitrous oxide and only 15% nitrogen, although the large and irreversible solubility of nitrous oxide in the solution made it impossible to determine with accuracy the true composition and amount formed. Dilution of the solution with water at any time up to four days caused the precipitation, in 75 to 85% yield, of short, brittle, near-white fibers, whereas powders were obtained when the isolation was deferred for a longer time. The total nitrogen content of the products, instead of decreasing as the reaction time was extended, increased from the starting value of 13.8% to about 15% within four to seven days. Although the later analyses could not be duplicated with precision because the samples deflagrated readily, they were those required by an aldehydo- or keto-cellulose mono-oxime substituted by 1.7 nitrate groups. Reductive acetylation gave a 71% yield of a brown powder with the nitrogen content expected for an oxycellulose substituted with 2 acetyl and 1 oxime–acetate groups, and the absence of nitrate in this product argued for the validity of the above interpretation. The "oxycellulose mono-oxime dinitrate" (Structure II, R = H) was soluble in numerous organic liquids, and was recovered unchanged after solution for several days in pyridine or pyridine containing free hydroxylamine. It followed from the latter observation that pyridine–hydroxylamine and pyridine – hydroxylamine hydrochloride both removed the same nitrate groups from cellulose trinitrate, although the mechanism was obviously different in the two cases.

In order to support the views just expressed as to the course taken by the two partial denitrations of cellulose trinitrate, much of the work was repeated with pyridine solutions of *o*-methylhydroxylamine and its hydrochloride. Oxime formation or the reverse could then be easily followed by analyses for the methoxyl group. Little color developed in the solutions, whose viscosities decreased even more slowly than in the comparable hydroxylamine experiments, but neither nitrogen nor nitrous oxide was evolved. Addition of water to the solutions after various times precipitated in all cases white fibers, whose nitrate and methoxyl substitutions are summarized in Fig. 1. Denitration obviously proceeded at

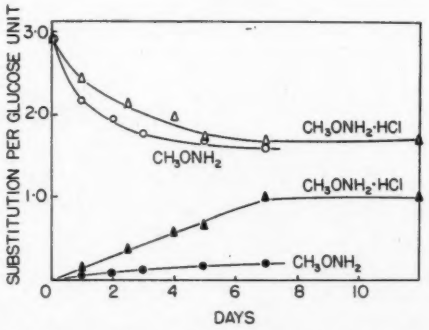


FIG. 1. Partial denitrations of 1 gm. cellulose trinitrate in 25 cc. of pyridine. With 5 gm. added *o*-methylhydroxylamine, ○, nitrate; and ●, methyloxime substitution. With 6 gm. added *o*-methylhydroxylamine hydrochloride, nitrate, △, and methyloxime substitution, ▲.

approximately the same rate and to the same extent in both reactions, but methyloxime rather than hydroxyl formation dominated only in presence of the hydrochloride. Methyloxime formation also lagged behind the denitration, because after the fifth day the former was only 68%, whereas the latter was practically 100% complete. Apart from its small content of methoxyl groups, the product from pyridine with free *o*-methylhydroxylamine proved to be similar to that from pyridine–hydroxylamine (Structure I) and was not systematically studied.

The "oxycellulose dinitrate *o*-methyloxime" acquired substitutions of about 1.7 nitrate and 1.0 oxime groups when isolated after five days (Structure II, R = CH_3) and further time in the reaction system did not alter these substitutions markedly. Since it was also recovered unchanged after solution for prolonged periods in pyridine or pyridine–hydroxylamine, the remaining nitrate groups were stable to both of these reagents. As with the other derivatives discussed, the *o*-methyloxime had unusually wide solubilities in organic liquids. Iodination of the substance with sodium iodide gave a poor yield of a brown powder that seemed highly degraded and contained 0.4 iodine atoms, 0.78 methyloxime, and 0.95 nitrate groups per glucose unit. This experiment suggested that some nitrate groups again occupied the primary alcohol positions and the methyloxime units were in the second or third positions, or were ketoximes. The stability of the methyloxime group toward acid hydrolysis also suggested that it was derived from a 2- or 3-keto-, rather than from a 6-aldehydo-cellulose. An attempt to denitrate the *o*-methyloxime with ammonium hydrosulphide resulted within two hours in a product soluble both in water and in alcohol. Lack of material made it necessary to discontinue the structural investigation at this point.

The intrinsic viscosities [η] noted in Column 4 of Table I were determined in

TABLE I

INTRINSIC VISCOSITIES OF "CELLULOSE DINITRATE" AND DERIVATIVES

	Days[a]	Substitution		Intrinsic viscosity[b]	Degree of polymerization[c]	Cleavage α %[d]
		NO_3	CH_3ON^-			
Original trinitrate	0	2.9	0	20	2000	0
In pyridine–hydroxylamine	3	2.6[e]	0	1.17	117	1.7
In pyridine–methylhydroxylamine hydrochloride	1	2.45	0.17	1.94	194	1.0
	2.5	2.14	0.41	0.59	59	3.3
	4	1.98	0.61	0.38	38	5.1
	12	1.70	1.01	0.18	18	10.5

[a] *Of preparation in pyridine–hydroxylamine or pyridine–methoxylamine hydrochloride solution.*

[b] *In n-butyl acetate at 25°C.*

[c] *Intrinsic viscosity × 100 (Ref. 27), uncorrected for variability in substitution (Ref. 8).*

[d] *When an infinite D.P. was assumed for original trinitrate, α % = 200/(D.P. + 1) for random cleavage (Ref. 21).*

[e] *After renitration without degradation (Ref. 5) from N, 10.4% to N, 13.1%.*

n-butyl acetate, which was a good solvent for all the derivatives discussed. Although the assumption required to translate intrinsic viscosities into average degrees of polymerization made the latter of doubtful accuracy, the percentages of glycosidic bonds which theoretically had to be cleaved in random fashion (Column 6) to give the observed values were maxima, because the calculation assumed that the original trinitrate was of infinite chain length. It was evident that the removal of an average of at least one nitrate group, and its replacement by a methyloxime or hydroxyl unit, per glucose residue was associated with the cleavage of 10% or less of the glycosidic bonds in the original cellulose trinitrate. Such cleavage was therefore not an integral step in the partial denitrations, but could be attributed to a side reaction of an unknown nature.

Although the mechanism by which hydroxylamine in pyridine reduced cellulose trinitrate to the "dinitrate" was not studied in detail, the reaction seemed analogous to others in which a nitro group was transferred to a compound containing a reactive hydrogen atom. Ethyl nitrate and potassium ethylate, for example, produced phenyl nitroacetic ester from ethyl phenyl acetate, and 3-nitrosopyrrole from pyrrole (32). The closest parallel found was the formation in up to 50% yield of nitrohydroxamic acid and ethanol from ethyl nitrate and hydroxylamine in presence of sodium ethylate (2). In the present case, the nitrohydroxamic acid and the large excess of hydroxylamine were probably responsible for the nitrogen formed.

$$EtONO_2 + H_2NOH \xrightarrow{NaOEt} NO_2HNOH + EtOH$$

$$NO_2NHOH + H_2NOH \longrightarrow N_2 + HNO_2 + 2H_2O$$

Pyridine was essential to the primary reaction, because cellulose trinitrate was recovered with undiminished nitrogen content after solution in ethylene glycol monomethyl ether containing an excess of hydroxylamine base. The lack of gas formation in the corresponding reaction with pyridine-*o*-methylhydroxylamine suggested that the intermediate NO_2NHOCH_3 was stable in the experimental conditions. This type of denitration, which was not of a redox nature and possibly involved the transfer of the nitronium NO_2^+ ion from oxygen to the nitrogen atom in hydroxylamine, was not included among the three alternative mechanisms for denitration recently elucidated by the extensive kinetic studies of Baker and Easty on simpler analogues (4).

The dominant reaction between the trinitrate and pyridine – hydroxylamine hydrochloride was assumed to be of the elimination type (4), first yielding a carbonyl group and the elements of nitrous acid, and

$$>CHONO_2 \longrightarrow >C = O + H - - NO_2$$

then the oxime and nitrous oxide, respectively, in presence of the excess hydroxylamine hydrochloride.

$$NH_2OH.HCl + H - - NO_2 \longrightarrow N_2O \uparrow + 2\,H_2O + HCl \quad (33)$$

It was unlikely that nitrous acid as such was actually formed, because the

solution gave a negative test for the nitrite ion, and because hydroxylamine hydrochloride and pyridinium nitrite were found not to react rapidly in pyridine solution. The test, however, was positive in the analogous reaction with *o*-methylhydroxylamine hydrochloride, and no gas was evolved, presumably because the intermediate, $HON = N - OCH_3$, was stable in pyridine. This substance was reported to decompose to nitrous oxide and methanol when in aqueous solution (7).

EXPERIMENTAL

Materials

De-waxed cotton linters, the gift of H. M. Spurlin and the Hercules Powder Company, were dried, nitrated for two hours at 5°C. in a phosphorus pentoxide – nitric acid mixture, and stabilized in aqueous ethanol, according to Berl's (5) directions. Storage of the cellulose trinitrate (N, 13.9%, or substitution 2.92; yield 96%) was over phosphorus pentoxide in a desiccator, and all manipulations of the dangerous explosive were made with care, particularly to avoid grinding fragments under the glass lid of a container. Later workers stored not more than 2-gm. samples in one vessel as an added precaution.

The hydrochlorides of hydroxylamine and *o*-methylhydroxylamine, together with *o*-methylhydroxylamine itself, were commercial C.P. samples. Free hydroxylamine was prepared by decomposing a suspension of 348 gm. of the hydrochloride in 300 cc. of butanol with a hot solution of 125 gm. of sodium in butanol (18), added as rapidly as was consistent with avoidance of an alkaline reaction. The unstable, white crystalline product, 105 gm. (65%), was promptly used, although it could be preserved for some time in a desiccator kept at − 10°C.

All pyridine was dried over barium oxide and the fraction boiling at 115° to 115.5°C. was used.

Analytical Methods

Total nitrogen was determined by either the Dumas (15), the macro- or micro-Kjeldahl (3) methods; nitrate nitrogen by a semimicro modification of the du Pont nitrometer method (13). The Viebock and Schwappach (9) estimation was used for methoxyl groups, and acetyl was determined as acetic acid after oxidizing the sample with chromic acid (22). To estimate iodine, 30 to 40 mgm. samples were saponified in aqueous potassium hydroxide (24), the iodide so formed was oxidized by bromine to iodate, and the latter was titrated iodometrically as described by Doering (12).

Relative viscosities, η_{rel}, were determined, at 25°C. in an Ostwald pipette, on solutions made by dissolving accurately-weighed 1 to 5 mgm. samples of the original nitrocellulose, or 25 to 100 mgm. samples of degraded specimens, in a weighed amount of pure *n*-butyl acetate. The solutions were accurately diluted until the quotient $(\eta_{rel} - 1)/C$ became independent of the concentration C%. This quotient was accepted as the intrinsic viscosity $[\eta]$ (Table I).

Gas Evolved from Cellulose Trinitrate – Hydroxylamine – Pyridine

A solution containing 5 gm. of crystalline hydroxylamine in 50 cc. of dry pyridine was run from a dropping funnel into a flask containing 2.0 gm. of cellulose trinitrate. While the solution was being introduced, a three-way stopcock

connecting the flask to a gas burette was open to the atmosphere. The stopcock was then turned to connect the burette, which had been filled with mercury and was equipped with a leveling bulb. The results, Table II, fitted a smooth curve and were thought to be precise to 2%.

TABLE II

EVOLUTION OF NITROGEN FROM CELLULOSE TRINITRATE IN PYRIDINE–HYDROXYLAMINE[a]

Hours	N_2 evolved		Hours	N_2 evolved	
	cc.[b]	moles[c]		cc.[b]	moles[c]
0.33	28	0.16	5.0	166	0.95
0.9	105	0.60	5.5	168	0.96
1.25	119	0.68	6.0	169	0.97
1.75	133	0.76	6.7	172	0.99
2.0	138	0.79	11.0	183	1.05
4.5	163	0.94			

[a] *Trinitrate, 2.0 gm., pyridine, 25 cc., and hydroxylamine, 5.0 gm. at room temperature.*

[b] *At 25°C. and 750 mm. pressure.*

[c] *Moles N_2 per glucose residue. Corrected for vapor pressure of pyridine at 25°C. (20 mm.).*

The gas was identified in a separate experiment in which 3.0 gm. of the trinitrate was placed in the reaction bulb of a du Pont nitrometer through the bottom opening. The leveling bulb containing mercury was attached and the reaction bulb was then evacuated until it had become completely filled with mercury and all air had been displaced from the fibers. A solution of 6 gm. of hydroxylamine in 75 cc. of pyridine was sucked into the reaction bulb from above and after 13 hr., when 240 cc. of gas had been evolved (1.00 mole per glucose unit), the bulb was connected to an Orsat apparatus (31). The pipettes in this apparatus contained 33% potassium hydroxide solution, 20% pyrogallol in 40% aqueous potassium hydroxide, and ammoniacal cuprous chloride for the absorption of carbon dioxide, oxygen, and carbon monoxide, respectively. Found: CO_2, 0.0, 0.0%; O_2, 0.1, 0.2%; CO, 0.7, 0.6%; residual gas, 99.2, 99.2%.

In a duplicate experiment, the gas from the reaction bulb was freed of pyridine vapor by passage through a trap cooled in solid carbon dioxide. A sample was then admitted at 524 mm. pressure and 25°C. to a highly evacuated bulb of 159 cc. capacity, whose increase of 0.1260 gm. in weight corresponded to a molecular weight of 28.2 for the gas. Another experiment gave a value of 28.6. The gas was therefore nitrogen (mol. wt. 28.0), since carbon monoxide was known to be present only in traces and since the gas was not condensed in a liquid air trap.

Preparation and Properties of Cellulose "Dinitrate"

Hydroxylamine, 100 gm., was dissolved in 600 cc. of dry pyridine and the solution was added to 30 gm. of dry cellulose trinitrate contained in a 2-liter flask. A white opaque gel formed and external cooling was necessary until the copious evolution of nitrogen slackened; thereafter the very viscous, pale yellow

solution was kept at 20°C. in the dark. After 76 hr., the yellow solution, now of somewhat lower viscosity, was slowly poured into 3 liters of mechanically stirred distilled water to precipitate the "dinitrate" as strong white fibers. The air-dried product was redissolved in 1 liter of dioxane–acetone (1:1), reprecipitated by pouring the solution into 6 liters of distilled water, thoroughly washed with water, and dried in the air. Final drying was *in vacuo* over phosphorus pentoxide. Found: N (macro-Kjeldahl), 10.47, 10.40; (nitrometer), 9.95, 9.94%. Calcd. for cellulose substituted with 1.68 nitrate and 0.08 oxime groups; total N, 10.43; nitrate N, 9.95%. The yield was 24 gm. or 98% based on the nitrogen content. Another sample, recovered after 11 hr. from the experiment described in Table II, had the following analysis. Found: N (macro-Kjeldahl), 10.60, 10.52; (nitrometer), 10.09, 10.08%. Calcd. for 1.70 nitrate and 0.08 oxime groups: total N, 10.55; nitrate N, 10.09%.

The "dinitrate" dissolved readily in acetone–dioxane (1:1), pyridine, ethanol–ether, butyl acetate, and with progressively less ease in dioxane, acetone, and glacial acetic acid. A 2-gm. sample, dissolved in 100 cc. of dioxane–ethanol–acetone containing 10 cc. of 10% aqueous sulphuric acid, was recovered with unchanged total nitrogen content (found: N, 10.0%) after 36 hr. at room temperature. Another sample, 3 gm., was recovered as cream-white fibers after solution for six days in a mixture containing 100 cc. of glacial acetic acid, 5 cc. of pyruvic acid, 10 cc. of dioxane, and 5 cc. of concentrated hydrochloric acid. Found: N (macro-Kjeldahl), 9.56, 9.50; (nitrometer), 9.18, 9.23%, corresponding to substitutions of 1.50 nitrate and 0.05 oxime groups.

To test for carbonyl groups (26), solutions of 1 gm. of the "dinitrate" in 100 cc. of ethanol–dioxane (1:1) were mixed with solutions of 2.3 gm. of *o*-methylhydroxylamine hydrochloride in 13 cc. of water buffered to pH 5.3 and to pH 3.5 with potassium hydroxide. The white fibers recovered in quantitative yield after 60 hr. at either pH still had the original nitrogen content. Found: N (macro-Kjeldahl), 10.25, 10.24%. A determination of methoxy content was unfortunately not carried out. When 1 gm. of the "dinitrate" was kept at room temperature for nine days in 50 cc. of pyridine containing 5 gm. of *o*-methylhydroxylamine hydrochloride, the white fibrous product contained OCH_3, 1.01, 0.99%. Another experiment, in which the "dinitrate" was heated with the hydrochloride in ethanol–ether at 60°C. for four hours, gave white fibers with OCH_3, 0.94%. A methyloxime substitution of 0.08 required OCH_3, 1.0%.

Cellulose "dinitrate", 8 gm., was shaken for two days with 40 cc. of ethanol and 280 cc. of ammonium hydrosulphide made by saturating ice-cold 5 *N* ammonia with hydrogen sulphide gas. The solution was 3.25 *M* with respect to sulphide ion. After recovery, the product was washed with water, ethanol, carbon disulphide, acetone, and was air-dried. The pale yellow fibers, yield 5.3 gm. or 98%, contained S, 1.36%; N, 0.66%. Renitration of the fibers with phosphorus pentoxide and nitric acid (5) gave cellulose trinitrate. Found: N (nitrometer), 13.8%.

A "reductive acetylation" (17) of the "dinitrate" was attempted by adding 1 gm. of powdered zinc to 0.5 gm. dissolved in 4 cc. of acetic anhydride and

0.5 cc. of trimethylamine. Heating on the steam bath and the addition of more zinc eventually gave a liquor with a negative diphenylamine test for nitrate groups. The product when reprecipitated from acetone solution into water consisted of 0.3 gm. of a brown powder, with acetyl 40.8%, corresponding to a cellulose acetate of substitution 2.52.

Acetylation of the "Dinitrate"

A 1-gm. sample was kept dissolved in 5 cc. of dry pyridine and 25 cc. of acetic anhydride for 24 hr. before the solution was poured into ice and water. The product after two reprecipitations from acetone solution into water occurred as long white fibers. Found: N (micro-Kjeldahl), 8.89, 8.85%. Calcd. for cellulose substituted with 1.68 nitrate, 0.08 oxime, and 1.0 acetyl groups, total N, 8.8%. The presence of the nitrate groups made the analysis for acetyl quite uncertain.

This nitrate–acetate was insoluble in dioxane and butyl acetate but dissolved readily in acetone; in contrast, the original "dinitrate" was soluble in the first two liquids but only sparingly so in the third.

Methylation of the "Dinitrate"

(*a*) A solution of 1 gm. in 60 cc. of pure dioxane and 25 cc. of ether containing 0.7 gm. of diazomethane was kept near 0°C. for one week, during which time some pressure developed in the container. An additional 20 cc. of the diazomethane solution and 7 cc. of 60% aqueous dioxane were added and two days later the methylation was stopped by the careful addition of acetic acid. After recovery, the long white fibers, 1.0 gm., contained OCH_3, 0.5%.

(*b*) A solution of 5.75 gm. of the "dinitrate" in 220 cc. of pure dioxane was shaken at room temperature for 24 hr. with 36 cc. of dimethyl sulphate and 36 cc. of 30% sodium hydroxide. No color developed. The mixture was poured into water and the white flocculent precipitate was recovered as brittle white fibers after reprecipitation from 5% acetone solution into water. Yield 4.8 gm. or about 85%. Found: N (micro-Kjeldahl), 9.91, 9.97; OCH_3, 11.7%. Calcd. for cellulose containing 1.73 nitrate, 0.08 methyloxime, and 0.88 methoxyl groups: total N, 9.94%; OCH_3, 11.7%. A smaller scale preparation, with N, 9.54, 9.46; OCH_3, 12.3, 12.3%, corresponded to substitutions of 1.62, 0.08, and 0.91, respectively.

Iodination of the "Dinitrate"

A 1-gm. sample dissolved in 35 cc. of acetone was mixed with 10 cc. of dioxane, 7 gm. of sodium iodide, and 6 cc. of allyl alcohol to remove free iodine as it was formed. The solution was heated at 100°C. for 18 hr. in a steel bomb, the resulting clear dark liquor was poured into water, and the gelatinous precipitate was washed free of iodine. After being dried, the product was a hard, brittle, gray-brown powder insoluble in acetone and dioxane. Found: N (micro-Kjeldahl), 2.43, 2.41; I, 35.8, 35.2%. Calcd. for cellulose with substitutions of 0.8 for iodine and 0.5 for nitrate groups: N, 2.42; I, 35.5%. The yield was 1.0 gm. or 89% on the above substitution.

Gas Evolved from Cellulose Trinitrate – Hydroxylamine Hydrochloride – Pyridine

The colorless gas was generated, in the apparatus previously used for studying the evolution of nitrogen, from 2 gm. of the trinitrate and a solution of 10 gm. of the hydrochloride in 50 cc. of pyridine. The rate of evolution was slower than

in the corresponding reaction with hydroxylamine itself, and the total amount, 0.8 to 1.1 moles per glucose unit, was dependent on the volume of pyridine used. One sample of the gas caused a glowing splint of wood to burst into flame, and another became only slightly yellow when mixed with an equal volume of pure nitric oxide. The gas was therefore nitrous oxide rather than nitrogen or oxygen.

An Orsat analysis (31) showed the gas to be somewhat soluble in the customary absorbing solutions, and 78% dissolved in an additional pipette containing ethanol. Commercial nitrous oxide was 92% soluble in ethanol under parallel conditions. In a density determination, 159 cc. contained 0.2058 gm. of the gas at 25°C. and 582 mm. pressure. Found: mol. wt., 41.4. Calcd. for 85% nitrous oxide and 15% nitrogen: mol. wt., 41.6. About 85% of the gas could be condensed in a receiver cooled in liquid air, and when recovered by evaporation this fraction had a molecular weight of 43.7, in good agreement with the value of 44.0 calculated for nitrous oxide.

Preparation of an "Oxycellulose Dinitrate Mono-oxime"

A solution of 60 gm. of hydroxylamine hydrochloride in 250 cc. of dry pyridine was added at 25°C. to 10 gm. of cellulose trinitrate in a flask, whose glass stopper was loosened frequently to relieve the pressure that developed. After four days the solution was poured into water and the yellow gum that separated was reprecipitated as brittle, short, cream-colored fibers from dioxane solution into water. Yield of dry product, 7.35 gm. or 85% based on the following analysis: N (Dumas) 15.0, 15.0%. Calcd. for a ketocellulose substituted with 1.7 nitrate and 1.0 oxime groups: total N, 15.0%. The sulphuric acid, even when ice-cold, used in the du Pont and Kjeldahl estimations caused the deflagration of the samples and the results ranged from 14.2 to 14.9%.

The oxime was soluble in dioxane, acetone, ethanol, acetic acid, butyl acetate, acetic anhydride, and pyridine. A 1-gm. sample, reductively acetylated (17) as already described, until nitrate-free by the diphenylamine test, gave a brown powder with N, 4.63, 4.63%. Calcd. for a ketocellulose substituted with 2.0 acetyl and 1.0 acetyloxime groups: total N, 4.54%. The yield was 0.85 gm. or 71%.

Preparation of "Oxycellulose Dinitrate o-Methyloxime"

Cellulose trinitrate, 9.5 gm., was allowed to react for seven days dissolved in 250 cc. of dry pyridine containing 60 gm. of *o*-methylhydroxylamine hydrochloride. The yellow solution when poured into water yielded a cream-colored, flocculent precipitate, which was washed thoroughly with distilled water and was purified by reprecipitation from dioxane. Yield, 8.5 gm. or 93% based on the following analysis. Found: N (macro-Kjeldahl), 14.1, 14.1; (Dumas), 14.2; OCH_3, 11.66, 11.75%. Calcd. for oxycellulose containing 1.68 nitrate and 1.0 methyloxime groups: total N, 14.1; OCH_3, 11.7%. A similar preparation yielded a product containing 1.70 nitrate and 0.97 methyloxime groups per glucose unit.

The substance was soluble in acetone, ethanol, dioxane, and butyl acetate. One-gram samples, shaken at room temperature in 25 cc. of *N* phosphoric acid for two days; in 20 cc. of dioxane containing 0.6 cc. of concentrated hydrochloric acid for one hour; and in 15 cc. of dioxane, 2 cc. of 85% phosphoric acid, and 4 cc. of water for 18 hr.; were recovered with methoxyl contents of 12.0, 12.0; 10.5,

10.5; and 11.5%, respectively. The oxime was therefore difficult to hydrolyze.

Iodination of the "o-Methyloxime Dinitrate"

A 0.8-gm. sample dissolved in 10 cc. of acetone was heated with 5 gm. of sodium iodide in a steel bomb at 100°C. for two hours (30). A second iodination of the solid residue, with 100 cc. of acetone and 10 gm. of sodium iodide, included 10 cc. of allyl alcohol to remove the free iodine that was formed. The undissolved, discolored product was extracted with benzene and was reprecipitated into water from solution in dioxane. Yield, 0.45 gm. of a brown powder that seemed highly degraded. Found: I, 18.3; OCH_3, 8.82, 8.75; N (micro-Kjeldahl), 8.77, 8.99%. Calcd. for cellulose with substitutions of 0.40 for iodine, 0.78 for methyloxime, and 0.95 for nitrate groups: I, 18.3; OCH_3, 8.8; total N, 8.8%.

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STRUCTURE OF A LEVAN PRODUCED BY *BACILLUS POLYMYXA*[1]

By Diarmuid Murphy[2]

ABSTRACT

A strain of *Bacillus polymyxa* has been shown to produce two different polysaccharides when grown on a yeast extract – salts – sucrose medium in the presence of calcium carbonate. One of these polysaccharides is a levan. Methylation and hydrolysis of this compound followed by chromatographic separation on a silica column gave 1:3:4-trimethyl-D-fructofuranose, 1:3:4:6-tetramethyl-D-fructofuranose, and 3:4-dimethyl-D-fructofuranose in the proportions 6:1.5:1 (by weight). A possible formula is suggested.

Cooper (8) has reported the production of levan by *Bacillus polymyxa* and related species and has proposed that this characteristic might be used in determinative bacteriology. No structural data have been reported on the levan of *B. polymyxa*, although such studies have been carried out on the levan of closely related species, such as *B. mesentericus* (11), and *B. subtilis* (10). Hibbert, Tipson, and Brauns (11) showed that the levans from both these organisms were essentially similar and could be regarded as polymerized 2:6-anhydrofructofuranose. The levan of *B. mesentericus* was reported (7) to consist of 10 to 12 contiguous fructofuranose units linked through the 2:6 positions. The molecular weight of such a polymer would be about 1600–2000, but, when determined by the method of Bergmann and Machemer (6), was actually 3800.

The levan from the strain of *B. polymyxa* used in this investigation is nonreducing and appears to be composed exclusively of fructofuranose units. Paper chromatography of the acid hydrolyzate in various solvents followed by spraying with urea oxalate showed fructose as the only sugar present. During the investigation, it was observed that colorimetric determination of the sugar in the oxalic acid hydrolyzate of the levan, using fructose as a standard (1), gave yields of 100% fructose. Using Nyn's (19) modification of Ost's cuprocarbonate reagent, the yield of fructose was 90.36%. Using the Somogyi copper reagent (26) with boiling for 15 min. and a fructose standard, the amount of fructose in the hydrolyzate was found to be 91.7%. The higher result with this reagent was undoubtedly due to the more vigorous heating employed. Palmer (21) found that *B. subtilis* levan on mild acid hydrolysis yielded 90 moles of fructose for each 100 moles of hexose in the levan. This effect was first observed in the levan, inulin, by Jackson and Goergen (14) who demonstrated a crystalline difructose anhydride in the mother liquors remaining after the removal of fructose and glucose obtained in the hydrolysis of purified inulin. Later, Jackson and McDonald (15) found two other difructose anhydrides in the mother liquors. The three anhydrides were nonreducing and had positive rotations. Jackson and McDonald found that, when inulin was hydrolyzed, only 94.8% of the theoretical carbohydrate could be accounted for as reducing sugar (91.8% as fructose, 3% as

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glucose). The rotation of hydrolyzed inulin solutions is also anomalous. Pure fructose (1 gm. in 100 ml. water) has a specific rotation of $-91.63°$ at 20°C. (20). Tanret (27) obtained a figure of $[\alpha]_D = -81.3°$ for inulin hydrolyzed with 10% hydrochloric acid. The major part of this difference in rotation must be ascribed to the difructose anhydrides. Solutions of *B. polymyxa* levan hydrolyzed with oxalic acid had a specific rotation of $[\alpha]_D^{25} = -83.5°$, a value well below that of a solution of fructose. Since paper chromatography revealed no sugar other than fructose in the levan hydrolyzate, the specific rotation and the reducing power values seem to show that difructose anhydrides occur among the hydrolysis products of the levan.

Periodate oxidation of the levan produced 1 mole of formic acid for each 22.7 hexose units (in 214 and 307 hr.), indicating a chain of 22–23 fructose residues with one reducing group (Fig. 1). The uptake of periodate in 24 hr. corresponded to 1.07 mole per hexose unit (constant value).

Methylation of the levan with dimethyl sulphate in alkali, followed by silver oxide and methyl iodide, gave a thick brown oil (42.87% methoxyl) which could not be fractionated. Hydrolysis of this product followed by separation of the components on a silica column (4) gave 3:4-dimethyl-, 1:3:4-trimethyl-, and 1:3:4:6-tetramethyl-D-fructofuranoses in the proportions of 1.5:6:1 by weight.

Anhydrofructofuranose units linked in the 2:6 position would account for the occurrence of 1:3:4-trimethyl-, and 1:3:4:6-tetramethyl-D-fructofuranoses among the products of hydrolysis of the methylated levan. The occurrence of 3:4-dimethyl-D-fructofuranose among the hydrolysis products of bacterial levans has apparently not been noted previously, although it occurs in the hydrolysis products of two other levans, such as avenarin (24), and triticin (1). Its occurrence in *B. polymyxa* levan could be accounted for by a branched-chain structure, the branches occurring in the 1 position (Fig. 1).

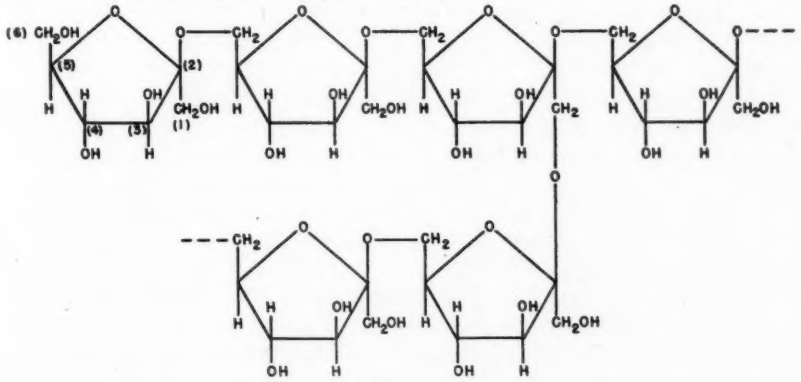

FIG. 1

There is, however, another possible explanation for the presence of 3:4-dimethyl-D-fructofuranose among the hydrolysis products of the methylated levan. It has been noted earlier that on hydrolysis of the levan only 90–91% of the

theoretical fructose could be accounted for by copper reduction. The rest of the fructose was presumably present as difructose anhydrides. In this levan, as in inulin, it is not known whether these anhydrides are present in the original molecule or whether they are formed only on hydrolysis. If they were present, either difructose anhydride 1 (1,2′:2,1′-di-D-fructofuranose anhydride) or difructose anhydride 111 (1,2′:2,3′-di-D-fructofuranose anhydride) give rise to 3:4-dimethyl-D-fructofuranose on methylation and hydrolysis. If these anhydride molecules occurred in the levan of *B. polymyxa* it would be necessary to assume that they were linked to the rest of the molecule through their 6:6′ positions. The molecule of difructose anhydride 111 linked in the 6:6′ position would, however, also yield 1:4-dimethyl-D-fructofuranose, which was not found among the hydrolysis products.

EXPERIMENTAL

Materials and Methods

The organism, *B. polymyxa*, strain C3(2),* was grown on the following medium: Difco yeast extract 0.5 gm., K_2HPO_4 0.05 gm., KH_2PO_4 0.05 gm., $MgSO_4.7H_20$ 0.02 gm., sucrose 7 gm., water 100 ml. One liter of medium was sterilized for 15 min. at 15 p.s.i. in 3-liter Fernbach flasks. When cool, 16 gm. of sterile commercial calcium carbonate was added. The inoculum was grown for 24 hr. on the same medium, without calcium carbonate, the flasks being shaken at 32°C. Five milliliters of inoculum was added to each Fernbach flask. The incubation temperature was 32.2°C. (90°F.) and the flasks were shaken twice every day with a time interval of eight hours. Reducing sugar was determined daily after the fifth day. When reducing sugar concentration fell to a constant level of 0.4% (seventh or eighth day) the fermentation was judged complete. The contents of the flasks were then pooled and heated to 85° or 90°, causing the calcium salts to settle out rapidly in a granular form. After centrifuging at 2000 r.p.m. the opalescent supernatant liquor was decanted and concentrated at 40–45°C. to one-third volume in an all-glass evaporator (2).

Extraction

Ethanol (95%) was added slowly, with constant stirring, to the concentrated solution. To obtain sharp separation of the various polysaccharides, stirring was stopped for five minutes after the addition of each aliquot of 150 or 200 ml. of ethanol. The first precipitate formed (after the addition of 1200 ml. of ethanol to 2 liters of the concentrate) was a compound high in ash and containing no fructose. This material will be the subject of a further communication. After the addition of another 1800 ml. of ethanol, a precipitate of levan was obtained. The yield of crude levan was about 10% by weight of the sugar used, or 20% of the fructose part of the sucrose molecule.

The levan was purified by treatment with tertiary amyl alcohol and chloroform (25) and obtained after freeze-drying, as a white powder (ash 0.86%, Kjeldahl nitrogen = 0.09%). It was readily soluble in water, and had $[\alpha]_D^{25} = -43°$ ($c = 1.042$) changing to $-83.5°$ when hydrolyzed for one hour at 100°C. in 1%

**From the Culture Collection of the Division of Applied Biology, National Research Council of Canada.*

oxalic acid. Unlike the levan triticin (1) the compound did not autohydrolyze on prolonged heating in water at 100°C. Paper chromatography of the hydrolyzate in a variety of solvents gave only one spot with the same R_f value as fructose and showing the characteristic greenish-blue color of ketoses when developed with urea oxalate at 115°C. The molecular weight ranged from 3300–4000, equivalent to 20–25 hexose units, as determined from the iodine number by the method of Bergmann and Machemer (6). Analytical figures corresponded to those of a compound with the empirical formula $(C_6H_{10}O_5)_n$ (found C = 44.03%, H = 6.65%, requires C = 44.44%, H = 6.17%).

Acetylation

The acetyl compound was prepared by three prolonged treatments with boiling pyridine and acetic anhydride. The mixture was poured into ice-water, filtered, washed well with ice-water, ethanol, and ether, and dried *in vacuo*. The compound could not be crystallized as it was not soluble in any available solvent. The crude well-washed compound softened at 180° and melted at 243–245°C. Analytical values corresponded to those of a triacetyl compound (found C = 49.76, 49.32%, H = 5.89, 5.83%, CH_3CO = 43.94%, $C_6H_7O_5$; $3CH_3CO$ requires C = 49.97%, H = 5.60%, CH_3CO = 44.7%).

Methylation

The levan was methylated (13) by treating it four times with dimethyl sulphate and sodium hydroxide and twice with silver oxide and methyl iodide. Twenty grams of levan gave 25 gm. of a dark brown gum which was dissolved in 250 ml. of acetone, refluxed with charcoal, and filtered. The resultant clear yellow solution did not deposit any crystals. The solution was then placed in a cold room (10°F.) for 10 days and aliquots of 250–300 ml. of 40–60° petrol ether were added at 24-hr. intervals. During this treatment a series of dark yellow oils of practically identical properties settled out. Their methoxyl content was 42.87% ($C_6H_7O_2.(OCH_3)_3$ requires 44.61%). The specific rotation in chloroform was $[\alpha]_D^{25} = -50.4°$ (c = 0.5%); in 72% ethanol it was $-45.1°$ (c = 1.72%). Hydrolysis of the compound followed by removal of the glycosides gave, on chromatography in butanol: water (1:1), three spots of R_f value 0.50, 0.73, and 0.80.

Hydrolysis of the Methylated Levan and Separation of the Products

Large-scale hydrolyses were carried out by dissolving 2 or 3 gm. of the compound in 130 ml. of redistilled 95% ethanol, adding 1.75 gm. oxalic acid in 47 ml. of water, and refluxing on a water-bath at 100°C. Hydrolysis was usually complete in eight or nine hours (constant rotation). The solution was brought to pH 7 with sodium bicarbonate, filtered from a small amount of tar, and concentrated in very slight vacuum to about 50 ml. Water was then added and the ethanol removed by continued distillation. Glycosides were hydrolyzed by heating at 90°C. for two hours with 1.1 ml. of concentrated hydrochloric acid. The solution was again neutralized with sodium bicarbonate and was then ready for chromatography by the method of Bell and Palmer (4), the precautions recommended by these workers being observed. However, no butanol was added to the chloroform for the elution of the 1:3:4-trimethyl-D-fructose from the silica column.

The 1:3:4:6-tetramethyl-D-fructose was removed first in toluene containing

0.33% by volume of ethanol. This solution was concentrated at normal pressure, in the presence of a little barium carbonate, to 50 ml. and extracted 18 times with 50-ml. aliquots of water. The aqueous solution was filtered and made to volume (1000 ml.). After suitable dilution the tetramethyl fructose was determined colorimetrically with anthrone (18) using synthetic 1:3:4:6-tetramethyl-D-fructofuranose (12) as the standard. Over the range chosen, plotting "concentration" against "2-log % transmission" gave a straight line.

The 1:3:4-trimethyl-D-fructose was eluted in chloroform. This solution was concentrated *in vacuo* (barium carbonate) at 35°C. leaving a pale yellow oil which was estimated gravimetrically, in a still of the type described by Bell (3), after drying in high vacuum over phosphorus pentoxide, or magnesium perchlorate and sodium hydroxide.

The 3:4-dimethyl-D-fructose left on the silica column was removed in methanol, the solvent evaporated at low temperature (barium carbonate), and the dimethyl compound transferred to a Bell-type still with warm dichlorethylene. The compound was obtained as a yellow oil and was determined gravimetrically after thorough drying.

As a result of three separate hydrolyses the 1:3:4:6-tetramethyl-, the 1:3:4-trimethyl-, and the 3:4-dimethyl-compounds were obtained in an almost exact proportion of 1:6:1.5 by weight. The purity of the compounds was demonstrated by paper chromatography.

Characterization of 1:3:4:6-*Tetramethyl-*D-*fructofuranose*

This compound, a pale yellow oil, was obtained by vacuum concentration and chloroform extraction of the aqueous solution used in the colorimetric determination. It was characterized by the following observations.

(1) *R_f value.*—In butanol–water (1:1) this was 0.80 for both the pure compound prepared from sucrose and the compound obtained from the levan. In tertiary amyl alcohol, ethanol, water (3:1:4) it was 0.78–0.80.

(2) *Methoxyl content.*—The first estimations were about 46%, probably owing to the hygroscopic nature of the compound. Drying *in vacuo* for 20 hr. before weighing gave values of 51.94 and 51.14% ($C_6H_8O_2.(OCH_3)_4$ requires 52.5%). Values reported in the literature vary from 49% (9) to 52% (22).

(3) *Refractive index.*—n_D^{25} on the redistilled vacuum-dried compound was 1.4516. Bell and Palmer (4) found 1.4506 (at 20°C.). Schlubach and Müller (23) give $n_D^{20} = 1.4509$.

(4) *Specific rotation.*—The vacuum-dried compound from the Bell still showed $[\alpha]_D^{25} = +28.63$ (water, $c = 1.426$). The compound after distillation *in vacuo* (153–6° at 0.75 mm.) showed the following values in water: 0 hr., + 16.98°; 4 hr., + 20.97°; 22 hr., + 22.56°. Schlubach and Müller (23) record a value of $[\alpha]_D^{20} = +31°$ (water).

Characterization of 1:3:4-*Trimethyl-*D-*fructose*

This compound crystallized only after long standing and after vigorous rubbing with a glass rod. Bell and Palmer (4) reported that their samples crystallized only on seeding. The values reported here, except the melting point, were obtained on the compound before crystallization.

(1) *R_f value.*—The R_f value of this compound in butanol–water (1:1) was consistently 0.68–0.70 (center of spot). Bell and Palmer report a value of 0.6 for their samples in the same solvent mixture (4). In tertiary amyl alcohol – ethanol – water (3:1:4) the value was 0.74.

(2) *Methoxyl content.*—This was found to be 41.69% on the vacuum-dried oil. ($C_6H_9O_3.(OCH_3)_3$ requires 41.89%).

(3) *Refractive index.*—n_D^{25} found was 1.4655. A value recorded in the literature (11) is $n_D^{20} = 1.4661$ for the compound in the liquid form.

(4) *Specific rotation.*—This was $[\alpha]_D^{25} = -53.47°$ (water, $c = 0.871$) for the vacuum-dried compound. On vacuum-distillation the compound gave the following values, 0 hr. $= -40.57°$ (water, $c = 0.769$), 23 hr. $= -48.14°$. Bell and Palmer (4) noted a similar effect. Using a thoroughly dried sample ($c = 5$) they found that the rotation changed from $-56.9°$ at 60 min. to $-61.6°$ (constant) at 68 hr. Schlubach and Sinh (24) give a value of $-47.6°$ ($c = 1$, water).

(5) *Periodate oxidation.*—Bell, Palmer, and Johns (5) have shown that 1 mole of 1:3:4-trimethyl-D-fructose yields 1 mole of formaldehyde when oxidized with sodium periodate at pH 7.5. They also suggested that this might be used as a means of testing the purity of samples of 1:3:4-trimethyl-D-fructose, since, under the conditions of the experiment, 1:3:4:6-tetramethyl-D-fructose is not oxidized. Our samples yielded the theoretical amount of formaldehyde, which was determined colorimetrically using chromotropic acid (16).

(6) *Melting point.*—The compound, recrystallized from petrol ether (40–60°) – carbon tetrachloride, softened at 72°C. and melted at 75–76°C. Attempts to prepare a trityl derivative from the oil were unsuccessful.

Characterization of 3:4-Dimethyl-D-fructose

This compound was obtained as a light yellow oil. On standing in a desiccator over magnesium perchlorate or phosphorus pentoxide it turned dark brown. A similar effect was noted by McDonald and Jackson (17). The following characteristics were observed:

(1) *R_f value.*—In butanol–water (1:1), this was consistently 0.48 to 0.52. A value of 0.4 has been reported for this compound in the same solvent mixture (4).

(2) *Methoxyl content.*—The highly dried compound contained 29.25% methoxyl ($C_6H_{10}O_4.(OCH_3)_2$ requires 29.8%).

(3) *Specific rotation.*—The specific rotation of the freshly prepared compound was $[\alpha]_D^{25} = -15.43°$ ($c = 0.584$, methanol), changing to $-17.33°$ in 24 hr. Schlubach and Müller (23) give $[\alpha]_D^{20} = -12.5°$ changing to $-18°$ in four hours ($c = 0.5$, methanol). It was necessary to estimate the specific rotation as soon as possible after removing the compound from the column and drying it *in vacuo*. The dark brown product obtained on standing gave strongly positive rotations in methanol, the value increasing with the age of the sample (values recorded were $[\alpha]_D^{25} = +15°$, $+31.5°$, and $+51.5°$).

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THE DECOMPOSITION OF HYPOCHLOROUS ACID[1]

By M. W. Lister

ABSTRACT

The rate of decomposition of hypochlorous acid has been measured in aqueous solution in the presence of much sodium hypochlorite. The rate is nearly independent of the hypochlorite concentration, and proportional to the square of the hypochlorous acid concentration. Hence the mechanism proposed is

$$2HOCl \rightarrow HCl + HClO_2 \text{ (both ionized)},$$
$$HOCl + ClO_2^- \rightarrow Cl^- + HClO_3 \text{ (ionized)}.$$

The first step is the slower. The reaction

$$HOCl + ClO^- \rightarrow Cl^- + HClO_2 \text{ (ionized)}$$

also occurs, but is much slower. Oxygen is also evolved, by a first order reaction. Values for the rate constants at different temperatures of all these reactions are given. Measurements are also reported on certain equilibria present in these solutions: the ionization of hypochlorous and chlorous acids, and the reaction $HOCl + H_3O^+ + Cl^- \rightleftharpoons Cl_2 + 2H_2O$.

Details of modified analytical methods for hypochlorite and chlorate in the presence of chlorite are given.

INTRODUCTION

Hypochlorous acid decomposes, as has long been known, either to hydrochloric and chloric acids, or to hydrochloric acid and oxygen. The mechanism of the former decomposition, in aqueous solution in the presence of hypochlorite ions, has been suggested (1,2) to be a trimolecular reaction:

$$2\ HOCl + ClO^- \rightarrow ClO_3^- + 2\ HCl \text{ (ionized)}.$$

Since the decomposition of the hypochlorite ion has been found (3) to be bimolecular, it seemed worth while to discover whether the decomposition of hypochlorous acid could not be fitted to some simpler scheme than the trimolecular reaction given above. The present work deals with the decomposition of hypochlorous acid in the presence of considerably higher concentrations of aqueous sodium hypochlorite than of hypochlorous acid, since this seemed to be the simplest way to distinguish between a mechanism involving hypochlorite ions in the slowest step, and one not doing so. As will be seen later it also has the advantage of allowing the relatively high rates to be followed for a longer time, and in addition the reactions can be carried out in solutions of virtually constant ionic strength. It is believed that the present work does show that the decomposition to chloric acid takes place in two stages, of which the slower is bimolecular; and that there is also an independent unimolecular reaction giving oxygen.

EXPERIMENTAL

The solution containing hypochlorous acid and sodium hypochlorite was stirred in a 1 liter flask immersed in a water thermostat, whose temperature could be maintained to 0.02°C. The flask was fitted with a mercury sealed stirrer, a side arm through which samples could be taken, and a capillary lead to a gas burette. The samples were at various times analyzed for sodium chloride, hypochlorite, chlorite, chlorate, hydroxide, and carbonate. For most of these analyses

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well-established methods are available, as outlined briefly below; but it was found that the analysis of hypochlorite and chlorate could present difficulties in the presence of chlorite. The methods finally adopted were as follows.

Sodium Hydroxide and Carbonate

To a 5 ml. sample, 20 ml. of 3% hydrogen peroxide was added to decompose hypochlorite.

$$ClO^- + H_2O_2 \rightarrow Cl^- + O_2 + H_2O\,.$$

The mixture was then titrated with hydrochloric acid in the usual way for a hydroxide–carbonate mixture, with first phenolphthalein and then bromcresol green as indicators. In the present work the carbonate content was always low, though not negligible.

Sodium Chloride

The hypochlorite in a 2 ml. sample was destroyed with hydrogen peroxide, and the total resulting chloride was titrated with silver nitrate by the Volhard method. This measures hypochlorite plus chloride, the latter being found by subtraction.

Sodium Hypochlorite or Hypochlorous Acid

Two milliliters were pipetted out and run into about 15 ml. of 1% sodium hydroxide. This was poured into a measured amount, usually 50 ml., of standardized 0.15*N* arsenious oxide solution, which had been saturated (after pipetting out) with sodium bicarbonate. Enough excess sodium bicarbonate was added to keep the solution saturated throughout the subsequent titration. The excess of arsenious oxide was then titrated with standard iodine solution.

Only the hypochlorite oxidizes the arsenious oxide under these conditions. The reason for the addition of the 1% sodium hydroxide is as follows. It was found that, if solutions containing sodium hypochlorite and considerable amounts of sodium chlorite were run directly into the arsenic solution, the analytical results were low and erratic; the error could be as much as 30%. The trouble appears to be that hypochlorous acid is liberated locally by the strong acid, arsenic acid, as it is formed, and this hypochlorous acid reacts with the chlorite as well as with the arsenious oxide. The sodium hydroxide prevents any local acidity, and it was in fact found that this method removed any detectable interference by added chlorite. Care must be taken to avoid so much sodium hydroxide that any iodine is converted to iodate in the titration; usually the titration reaction liberates so much acid that there is no danger of this.

It is advised in earlier work (5) on this titration not to use too large an excess of arsenious oxide, as chlorite may react slightly with the larger amount of iodide formed in the titration. This will usually not be very important, as it was found that the apparent hypochlorite content of a pure sodium chlorite solution (0.5*M*) was only increased from 0.0001*N* to 0.0015*N* (or 0.00075*M*) when using first 5 ml. and then 25 ml. of 0.15*N* arsenious oxide.

Sodium Chlorite

Addition of potassium iodide and hydrochloric acid to a sample liberates iodine equivalent to the hypochlorite plus chlorite. This was titrated with thiosulphate.

Sodium Chlorate

Two milliliters of the solution was added to excess arsenious oxide solution, followed by 2 ml. of 0.008*M* iodine monochloride solution in 6*M* hydrochloric acid and 13 ml. of concentrated hydrochloric acid. The mixture was boiled briefly and the excess arsenious oxide titrated with potassium bromate using methyl orange as indicator. This measures the sum of hypochlorite, chlorite, and chlorate, the individual contributions being found by subtraction.

It is essential to add the iodine monochloride, because otherwise chlorine dioxide which is formed reacts too slowly with the arsenious oxide, and is partly lost during boiling. The iodine monochloride catalyzes this reaction; without it the results could be 3–4% low.

Measurement of Equilibria and Hypochlorous Acid Content

The general method of preparing solutions for the kinetic runs was to add a known amount of concentrated hydrochloric acid to an initially alkaline hypochlorite solution. It was essential to know certain equilibrium constants before the amount of hypochlorous acid liberated could be calculated. In general the hydrochloric acid reacts first with the sodium hydroxide in the mixture, then with the sodium carbonate as far as bicarbonate, and then liberates hypochlorous acid; but there is some overlapping.

Various values for the ionization constant of hypochlorous acid appear in the literature, the average being about 3×10^{-8}. This was checked by diluting the hypochlorite solution to about 0.25*M*, and titrating it with 0.1*N* sulphuric or hydrochloric acids; the titration was followed with a pH-meter. By plotting the slope, $d\text{pH}/dv$, where v is the volume of acid, against v, the mid-point where the slope is a minimum was obtained. At this point, as with any other buffer solution, $[\text{HOCl}] = [\text{ClO}^-]$; both titrations agreed that this was at a pH of 7.42, so that the ionization constant of hypochlorous acid is 3.8×10^{-8} at 27°C.

When excess acid was added so that the pH fell below about 3, the pH deviated from the calculated values, and the extent of this deviation agreed with the assumption that the reaction (4)

$$\text{HOCl} + \text{H}_3\text{O}^+ + \text{Cl}^- \rightleftharpoons \text{Cl}_2 + 2\ \text{H}_2\text{O}$$

was occurring reversibly, with an equilibrium constant

$$K = \frac{[\text{H}_3\text{O}^+] \cdot [\text{Cl}^-] \cdot [\text{HOCl}]}{[\text{Cl}_2]} = 5.5 \pm 0.3 \times 10^{-4} \text{ at } 27°\text{C}.$$

The dissociation constant of chlorous acid was measured similarly and gave a value of 1.01×10^{-2} at 23°C. These last two constants meant that virtually no chlorine or chlorous acid was present in the solutions being investigated.

As mentioned above the solutions used were prepared by adding hydrochloric acid to an alkaline hypochlorite solution. The acid was added from a microburette, graduated in 0.01 ml., with its tip dipping well below a weighed amount (about 800 ml.) of the sodium hypochlorite solution, which was kept well stirred. About 20 ml. of hydrochloric acid were added. At the start, and at two or three other points during the addition, samples of the solution were pipetted out; after addition of hydrogen peroxide these were titrated with 0.1*N* hydrochloric acid

to a phenolphthalein end point. By plotting the results of these titrations it was possible to extrapolate with considerable accuracy to find the volume of concentrated hydrochloric acid needed just to reduce the apparent sodium hydroxide content to zero. The word 'apparent' is used, because we have not yet made allowances for any reagent blank, or checked that this method does give exactly the sodium hydroxide concentration. In general a small excess of acid was added.

As the hypochlorous acid concentrations were generally between 0.01*M* and 0.05*M*, it was necessary to know them with considerable accuracy. The idea of simply measuring the pH was abandoned as not accurate enough, at least with the apparatus available. Direct calculation from the 0.1*N* hydrochloric acid titers is possible, but open to uncertainty; firstly because there was a trace of acid in the hydrogen peroxide, and secondly because the end point observed by the change of color of phenolphthalein, while certainly close to the true end point, might not be exactly at it. The following slightly indirect method was finally adopted to find the hypochlorous acid concentrations, because it only required a moderately accurate knowledge of the initial sodium hydroxide concentration, and avoided the question of the acid content of the hydrogen peroxide.

Five milliliters of the initial alkaline hypochlorite were pipetted out (and weighed as a check), diluted with 20 ml. of water, and titrated with 0.1027*N* hydrochloric acid; the titration was followed with a pH-meter. The resulting curve of pH against volume of acid gives a fairly sharp inflection point corresponding to the conversion of sodium hydroxide to chloride and sodium carbonate to bicarbonate; thereafter the curve falls slowly again as hypochlorous acid is formed. The carbonate concentration was initially 0.019*M* and the hypochlorite concentration 1.20*M*; using these values a pH curve was calculated that agreed well with the observed one; it had an inflection at a pH of 10.29, while the observed inflection was at 10.26. By superposing the two curves it was possible to find the sodium hydroxide content of the initial solution. The volume of 0.1027*N* hydrochloric acid for the usual titration with hydrogen peroxide and phenolphthalein was now found, and compared with the volume required to reach the inflection point above. Per liter of solution the inflection point (in absence of hydrogen peroxide) was reached when 10.4 milliequivalents of acid had been added beyond that necessary to neutralize the sodium hydroxide (also in absence of hydrogen peroxide); the phenolphthalein end point (i.e. when a sample plus hydrogen peroxide and phenolphthalein just required no 0.1*N* hydrochloric acid to give the color change of phenolphthalein) was reached in another 6.4, or a total of 16.8, milliequivalents.

The result of adding concentrated hydrochloric acid to the undiluted hypochlorite solution was now calculated. From this a curve could be drawn relating amount of acid added to the concentration of hypochlorous acid produced. The titration (with hydrogen peroxide) had shown that 333.5 milliequivalents of hydrochloric acid per liter of hypochlorite solution were needed to reach the phenolphthalein end point, and as this is 16.8 milliequivalents beyond that just required to neutralize the sodium hydroxide, the above curve could be redrawn

to relate hypochlorous acid concentration to the ratio of total acid added to that necessary to reach the phenolphthalein end point. A few of the calculated points are given in Table I to show the method; these are for 0.019*M* carbonate and

TABLE I

pH	$[CO_3^{--}]$	$[HCO_3^-]$	$[H_2CO_3]$	$[ClO^-]$	[HOCl]	[NaOH]	Acid	Ratio
11.0	0.01584	0.00316	–	1.2	0.00032	0.00100	0.00248	0.957
10.6	0.01267	0.00633	–	1.2	0.00079	0.00040	0.00672	0.970
10.2	0.00839	0.01061	–	1.198	0.00200	0.00016	0.01245	0.987
9.8	0.00460	0.01440	–	1.195	0.00499	0.00006	0.01933	1.008
9.4	0.00212	0.01686	0.00002	1.188	0.01247	0.00003	0.02934	1.038
9.0	0.00091	0.01804	0.00005	1.169	0.03083	0.00001	0.04896	1.096
8.6	0.00038	0.01849	0.00013	1.125	0.07418	–	0.09293	1.228

1.2*M* hypochlorite. All the concentrations in Table I are in moles per liter; under "acid" is given the amount of hydrochloric acid added beyond that equivalent to the initial sodium hydroxide; under "ratio" is given the ratio of total acid to that needed to reach the phenolphthalein end point. The dissociation constants of carbonic acid were taken to be $10^{-6.46}$ and $10^{-10.30}$. As regards the accuracy of this method, the ratio in the last column of Table I could be determined to 0.001; in the region of hypochlorous acid concentrations used, this would mean an error of 5%. This calculation was repeated for other carbonate concentrations, but, as these are low, it was evident that a moderate error in the carbonate concentration would not have much effect on the estimated hypochlorous acid concentration. Similar calculations were made for lower hypochlorite concentrations, and these were used as needed; as is to be expected, for a given amount of acid added, the hypochlorous acid falls only slowly as the hypochlorite decreases. A fall of 50% in the hypochlorite only leads to a 3 to 4% fall in the hypochlorous acid. Thus it can be fairly concluded that the main error in estimating hypochlorous acid concentrations is the 5% possible error from the volume of acid added. While this is not very great accuracy, it is difficult to be more precise in these solutions. It is however easily accurate enough for a determination of the mechanism, and of moderately accurate rate constants. It should be added that, while the above calculations only apply strictly to about 25°C., they are close enough at other temperatures provided the ionization constants of hypochlorous and carbonic acids change somewhat similarly with temperature.

RESULTS

The initial alkaline hypochlorite solution had an ionic strength of 3.79; after addition of hydrochloric acid this was reduced to close to 3.70, and all runs were done at this ionic strength. The ionic strength will not alter as the reaction proceeds.

Table II gives the analytical results on the various runs; the concentrations are in moles per liter, except under "total oxidizer", where is given the total oxidizing power of the solution expressed as a normality, i.e.

$$2[ClO^-] + 4[ClO_2^-] + 6[ClO_3^-].$$

TABLE II

Run No.	Temp., °C.	Acid added	Time (min.)	$[ClO^-]$, M	$[ClO_2^-]$, M	$[ClO_3^-]$, M	Total oxidizer, N
1	30	1.074	0	1.271	0.005	0.124	3.304
			61	1.202	–	–	–
			126.5	1.132	–	–	–
			213	1.038	–	–	–
			282	0.965	–	–	–
			475	0.761	–	–	–
			593	0.644	–	–	3.294
2	30	1.118	0	1.219	0.0045	0.142	3.309
			67	1.069	–	–	–
			129	0.927	–	–	–
			264	0.630	–	–	–
			413	0.344	0.001	0.431	3.279
3	30	1.150	0	1.225	0.002	0.142	3.308
			34	1.102	–	–	–
			93.5	0.899	–	–	–
			123	0.794	–	–	–
			152	0.687	–	–	–
4	30	1.044	0	1.285	0.0025	0.123	3.314
			43	1.268	–	–	–
			84	1.253	–	–	–
5	30	1.043	0	0.965	–	–	–
			68	0.939	–	–	–
6	35	1.044	0	1.229	0.007	–	–
			38	1.209	–	–	–
			114	1.168	–	–	–
7	35	1.043	0	1.066	–	–	–
			39	1.044	0.003	–	–
			101	1.006	–	–	–
			146	0.976	–	–	–
8	40	1.096	0	1.160	0.003	0.161	3.297
			53.5	0.980	0.003	0.220	3.290
			104	0.817	0.0025	0.274	3.284
			165	0.626	0.003	0.396	3.270
9	40	1.075	0	1.266	0.003	0.126	3.298
			62	1.146	0.005	–	–
			120	1.032	0.004	–	–
			224	0.841	0.004	–	–
			298	0.712	–	–	–
			349.5	0.625	0.004	0.333	3.263
10	40	1.179	0	1.042	0.002	0.200	3.283
			34	0.592	–	–	–
			55	0.367	–	–	–
11	40	1.044	0	1.146	0.006	–	–
			35.5	1.111	–	–	–
			86	1.072	–	–	–
			119.5	1.046	–	–	–
12	40	1.043	0	1.241	0.006	0.132	3.299
			93.5	1.155	–	–	–
			126	1.123	–	–	–
13	40	1.002	0	1.126	0.0065	0.168	3.288
			512	1.070	0.007	–	–
			1290	0.989	0.0055	0.211	3.267
14	50	1.057	0	1.160	0.0085	0.150	3.254
			52	0.984	0.0095	0.205	3.238
			104	0.816	0.0075	–	–
			144	0.688	–	–	–

This is a check on the oxygen evolved, since this alone reduces the total oxidizing normality. Under "acid added" is given the ratio of total hydrochloric acid to that needed to reduce the titer with phenolphthalein to zero, i.e. the same as the last column of Table I.

The results in Table II show that the rate of disappearance of hypochlorite is in general nearly constant (Fig. 1). This is to be expected if the slowest step

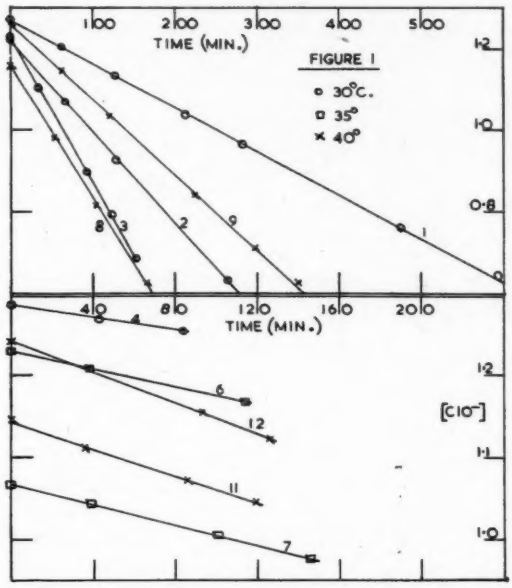

FIG. 1.

does not involve hypochlorite ions; the concentration of hypochlorous acid itself falls only very slowly as the chlorous and chloric acids formed rapidly regenerate hypochlorous acid. Table III gives various quantities calculated from the results of Table II. First are given the hypochlorous acid concentrations calculated as described above; then the mean hypochlorite ion concentrations over any time interval, corrected for the part of the total hypochlorite (as measured analytically) present as hypochlorous acid. Next are given the rates of disappearance of hypochlorite, corrected for the small amount of decomposition that occurs when free alkali is present, and which is due to the ion, not the acid. It is the relative constancy of these rates that show that hypochlorite ions are not directly involved. Lastly, to show the order of the reaction with respect to hypochlorous acid, the rates divided by the concentration are given under "K(1st order)", and divided by the concentration squared under "K(2nd order)".

The results of Table III show that the rate is independent of the hypochlorite ion concentration, and are most consistent with a second order reaction in hypochlorous acid; it can easily be checked that higher orders give worse constants. There is a certain drift in the second order constant, and this is attributed to a reaction between hypochlorous acid and hypochlorite ion. These results will be discussed later after the data on oxygen evolution have been given. Table IV gives the rates of oxygen evolution in milliliters of oxygen at N.T.P. per liter of solution; these rates are corrected for the slow evolution persisting even in alkaline solution which is due to hypochlorite ion. Since these rates agree best with a first order reaction in hypochlorous acid, the last column gives the first

TABLE III

Run No.	Temp., °C.	[HOCl], *M*	[ClO⁻], *M*	Rate, gm-moles/liter/min.	*K*(1st order)	*K*(2nd order)	$\frac{[ClO^-]}{[HOCl]}$
1	30	0.0241	1.212	1.11×10^{-3}	0.046	1.91	50
		0.0240	1.143	1.05	0.044	1.83	48
		0.0238	1.061	1.07	0.045	1.89	48.5
		0.0237	0.977	1.05	0.044	1.87	41
		0.0235	0.839	1.05	0.045	1.90	38
		0.0232	0.679	0.98	0.042	1.81	29
2	30	0.0376	1.106	2.23×10^{-3}	0.059	1.57	29.5
		0.0375	0.960	2.27	0.061	1.61	25.5
		0.0373	0.741	2.19	0.059	1.57	20
		0.0370	0.450	1.01	0.052	1.40	12
3	30	0.0486	1.115	3.59×10^{-3}	0.074	1.52	23
		0.0484	0.930	3.39	0.070	1.45	19
		0.0482	0.798	3.52	0.073	1.52	16.5
		0.0481	0.692	3.69	0.077	1.60	14.5
4	30	0.0145	1.261	3.72×10^{-4}	0.026	1.77	87
		0.0145	1.245	3.66	0.025	1.74	86
5	30	0.0138	0.938	3.74×10^{-4}	0.027	1.98	68
6	35	0.0144	1.204	4.94×10^{-4}	0.036	2.47	
		0.0144	1.174	5.27	0.038	2.66	
7	35	0.0139	1.041	5.23×10^{-4}	0.038	2.71	
		0.0138	1.011	5.86	0.043	3.07	
		0.0138	0.977	5.51	0.040	2.89	
8	40	0.0308	1.039	3.20×10^{-3}	0.107	3.45	34
		0.0307	0.867	3.17	0.104	3.37	28
		0.0305	0.690	3.07	0.101	3.30	22.5
9	40	0.0240	1.182	1.88×10^{-3}	0.078	3.26	49.5
		0.0239	1.065	1.91	0.080	3.34	44.5
		0.0236	0.912	1.79	0.076	3.22	38.5
		0.0234	0.753	1.70	0.073	3.11	32
		0.0232	0.646	1.65	0.071	3.07	28
10	40	0.0576	0.759	1.30×10^{-3}	0.226	3.92	13
		0.0572	0.423	1.06	0.185	3.24	7.5
11	40	0.0143	1.114	9.35×10^{-4}	0.065	4.57	78
		0.0142	1.078	9.27	0.065	4.60	76
		0.0142	1.025	7.91	0.053	3.75	72
12	40	0.0142	1.184	8.81×10^{-4}	0.062	4.37	83.5
		0.0140	1.125	9.47	0.068	4.83	80.5
13	40	0.00370	1.093	0.87×10^{-4}	0.024	6.35	295
		0.00356	1.025	0.83	0.023	6.54	288
14	50	0.0181	1.054	3.23×10^{-3}	0.178	9.86	
		0.0179	0.882	3.11	0.174	9.71	
		0.0177	0.734	3.08	0.174	9.83	

order rate constant, that is, the oxygen rates in gram-atoms per minute per liter of solution divided by the hypochlorous acid concentrations.

DISCUSSION OF RESULTS

The only mechanism for the decomposition of hypochlorous acid that seems to be compatible with these results is:

$$2\ HOCl \rightarrow HCl + HClO_2 \text{ (both ionized)} \qquad K_1$$

followed by

$$HOCl + ClO_2^- \rightarrow Cl^- + HClO_3 \text{ (ionized)}. \qquad K_2$$

The second stage is faster than the first. Any hydrochloric, chlorous, or chloric acids formed will rapidly ionize and regenerate an equivalent amount of hypochlorous acid. Hence the hypochlorous acid concentration, and the rate of

TABLE IV

Run No.	Temp., °C.	[HOCl], *M*	[ClO⁻], *M*	Rate (corr.), ml./min.	Rate/[HOCl]
1	30	0.0240	1.17	0.108	4.0×10^{-4}
		0.0233	0.70	0.142	5.4
2	30	0.03765	1.14	0.163	3.9
		0.0370	0.48	0.151	3.65
3	30	0.0484	1.00	0.279	5.15
15	30	0.00995	1.27	0.056	5.0
6	35	0.0144	1.20	0.125	7.8
8	40	0.0308	1.07	0.531	15.4
		0.0301	0.39	0.466	13.8
9	40	0.0236	0.94	0.370	14.0
		0.0234	0.78	0.380	14.5
		0.0232	0.67	0.359	13.8
11	40	0.0142	1.09	0.178	11.2
12	40	0.0141	1.17	0.185	11.7

decomposition should be nearly constant, as was found. This constancy excludes any mechanism involving hypochlorite ions directly. The reaction is second order in hypochlorous acid as was found, and this is also supported by the fact that a small concentration of chlorite or chlorous acid was always present. The second order constants given in Table III do show a certain drift with hypochlorous acid concentration; or, to put it slightly differently, they show a slow rise as the ratio of hypochlorite to hypochlorous acid rises. This is most simply explained by supposing that the reaction

$$HOCl + ClO^- \rightarrow ClO_2^- + HCl \text{ (ionized)} \qquad K_3$$

contributes a small amount to the total decomposition. Since the reaction giving oxygen is a first order one, it can be provisionally written

$$HOCl \rightarrow HCl \text{ (ionized)} + \tfrac{1}{2}O_2, \qquad K_0$$

though we must suppose that there is some rapid second stage converting an oxygen atom to a molecule. These reactions would give the rate equations:

$$\frac{d[ClO^-]}{dt} = -2K_1[HOCl]^2 - K_2[HOCl].\,[ClO_2^-] - 2K_3[HOCl].\,[ClO^-] - K_0[HOCl];$$

$$\frac{d[ClO_2^-]}{dt} = K_1[HOCl]^2 - K_2[HOCl]\,.\,[ClO_2^-] + K_3[HOCl]\,.\,[ClO^-]\,.$$

In order to apply these equations it can be assumed, as is confirmed by analysis, that the chlorite concentration is practically constant; it is formed in the first stage and used up in the second stage. With this simplification the first equation becomes:

$$\frac{d[ClO^-]}{dt} = -3K_1[HOCl]^2 - 3K_3[HOCl] \cdot [ClO^-] - K_0[HOCl] ;$$

and the stationary chlorite concentration is given by

$$[ClO_2^-] = \frac{K_1}{K_2}[HOCl] + \frac{K_3}{K_2}[ClO^-] .$$

The rates of gas evolution show that K_0 is relatively small; ignoring K_0 as a first approximation, the rate equation can be put in the form:

$$\text{Rate}/[HOCl]^2 = 3K_1 + 3K_3[ClO^-]/[HOCl] .$$

This shows that the last column in Table III represents $3K_1 + 3K_3[ClO^-]/[HOCl]$; if we plot rate/$[HOCl]^2$ against $[ClO^-]/[HOCl]$, (Fig. 2), the points cluster

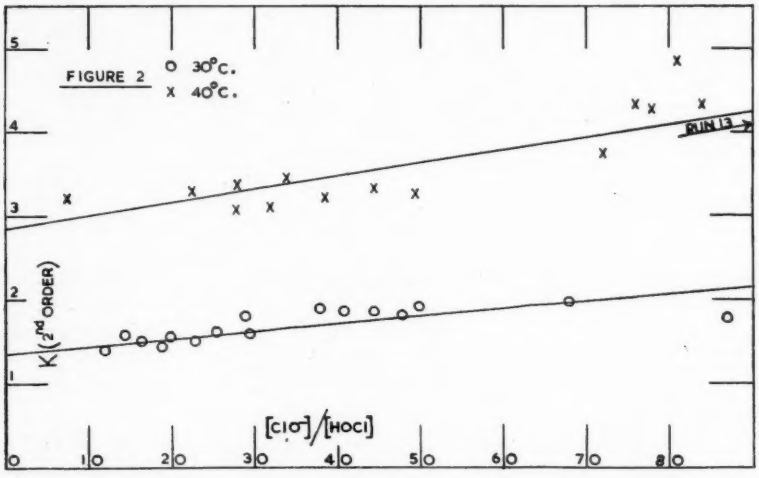

FIG. 2.

around a slowly rising line which gives the following values for the constants:

Temp.:	40°	30°C.
K_1:	0.95	0.45
K_2:	0.005	0.003

The units of concentration are gram-molecules per liter, and time is in minutes. Since relatively small errors in the analytical measurements would lead to considerable errors in the derived constants, the number of significant figures given are probably all that are justified. K_2 can be evaluated from the equation for the chlorite concentration, but the actual chlorite content is so low that the accuracy is low. The chlorite analyses give mean values for K_2 of 4 at 30°C., and 8 at 40°C. An attempt to confirm these values by adding sodium chlorite to a run failed because almost all the chlorite had reacted before the first analysis could be made; this run merely checked that K_2 is large.

The results for K_1 lead to an activation energy of 15 kcal. for the first stage. This value was checked more carefully by two series of runs at 30°C.,35°C., and

40°C. in which the same solution was measured at these three temperatures (runs 4,6,11 and 12,7,5). A plot of $\log(\text{rate}/[\text{HOCl}]^2)$ against $1/T$ extrapolates reasonably well to the value from run 14 at 50°C., and gives an activation energy of 15.7 kcal. This would be slightly high if the $HOCl + ClO^-$ reaction makes some contribution to the rate, since this has presumably a somewhat higher activation energy as its rate constant is lower. The general conclusion must be that the activation energy of the first stage is $15\frac{1}{2}$ kcal., with a possible error of 0.5 kcal No very useful estimates of activation energy can be made from K_2 and K_3.

The mean values for K_0, obtained by averaging the average values for each run, are:

Temp.:	30°	35°	40°C.
K_0:	4.65	7.8	12.9×10^{-4} min.$^{-1}$

These give an activation energy of 19 kcal. for the reaction to oxygen. The details of this reaction remain somewhat uncertain, since it is first order, but the product is molecular oxygen; perhaps the most plausible suggestion is that hydrogen peroxide is formed and that this reacts rapidly with hypochlorite ions:

$$HOCl + H_2O \rightarrow HCl + H_2O_2 \text{ (slow)},$$

$$H_2O_2 + ClO^- \rightarrow Cl^- + O_2 + H_2O \text{ (rapid)}.$$

It will be seen that the rate of oxygen formation is independent of the hypochlorite ion concentration, thus excluding the possibility that the two steps given above are really combined in a single reaction.

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PHASE TRANSITIONS IN MULTIMOLECULAR LAYERS OF ADSORBED NITROGEN[1]

By J. A. Morrison, L. E. Drain,[2] and J. S. Dugdale[2]

ABSTRACT

The heat capacity of nitrogen adsorbed on titanium dioxide has been measured for amounts adsorbed corresponding to 2.2, 3.1, 4.0, and 4.8 molecular layers in the temperature range 14° to 75°K. The occurrence in the adsorbed films of melting and of the transition in the solid phase of nitrogen is shown by maxima in the heat capacity. The melting process is completely reversible and takes place at temperatures below the normal melting point. The solid phase transition does not occur reversibly, the magnitude of the anomaly in the heat capacity depending upon the extent to which the system has been cooled prior to the measurement of the heat capacity. The experimental results are discussed in terms of current thermodynamic treatments of phase transitions in adsorbed films.

INTRODUCTION

A number of instances of melting in adsorbed films have been described in the literature. Patrick and Kemper (20) have discussed the melting of water, naphthalene, benzene, and *p*-nitrotoluene adsorbed on silica gel. Other evidence for melting of substances adsorbed on silica gel has been given by Higuti (8), by Brown and Foster (3), and by Iwakami (11). In addition, Batchelor and Foster (1) have found that the melting point of dioxane adsorbed on ferric oxide gel occurred below that of the bulk substance. Several attempts have been made to calculate the lowering of the melting point in the adsorbed phase with the assumption that the effect was due to adsorption in capillary spaces (1, 21, 9). This hypothesis is reasonable enough for porous solids. On the other hand, experiments which have recently been made with argon adsorbed on crystalline titanium dioxide (19) show a similar lowering of the melting point. It seems unlikely that in this system capillary condensation plays any important part.

Also of interest is the occurrence of the λ-point in films of helium adsorbed on nonporous solids, the experimental evidence coming from heat capacity measurements (6, 14), and from flow experiments (12, 13, 2).

In this paper the behavior of the phase transitions in nitrogen adsorbed on rutile is described and discussed with special reference to the possible coexistence of two surface phases, as has been proposed by Meyer and Long (15).* Besides the results to be given here, additional values of the thermodynamic functions of nitrogen adsorbed at concentrations corresponding to less than about two layers have been obtained, but these do not show phase transitions and will be discussed elsewhere. Brief mention is made of some results for argon adsorbed on rutile, not given previously.

EXPERIMENTAL

The calorimeter assembly used for the experiments and the calculation of the

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various thermodynamic functions from the experimental results have been described (17, 18, 5). In work with adsorbed argon it had been established (18) that physically adsorbed gas could be removed completely from the calorimeter system by pumping at room temperature. Therefore, the titanium dioxide in the calorimeter was not baked before the measurements with nitrogen were begun.

As has been noted previously (5), the main experimental difficulty encountered in the measurement of the heat capacity at higher surface coverages is distillation of material from the calorimeter to the filling tube during the cooling operation. Before starting a series of heat capacity measurements it was necessary to ensure that there was no gas condensed in the tube. To achieve this for the range above 50°K., the calorimeter was cooled to 50°K. with solid nitrogen in the cryostat, then thermally isolated and left overnight with the cryostat a few degrees warmer. This treatment was found to be sufficient to distill any nitrogen solidified in the tube back into the calorimeter. For the region below 50°K. a rather different technique had to be adopted because if nitrogen solidified in the tube during the cooling operation it could not be distilled out afterwards owing to the very low vapor pressure. It was necessary then to prevent condensation during cooling by keeping the tube and the top of the shield warmer than the calorimeter. With liquid hydrogen alone in the inner container of the cryostat (Fig. 1 of Reference 17) this was impossible. However, by leaving some solid nitrogen in the inner container and adding liquid hydrogen in small amounts the cooling process could be controlled easily. On the average the calorimeter was cooled at the rate of about 6° per hour. This slow cooling also had the advantage that equilibrium was maintained within the calorimeter—there was no danger of nitrogen solidifying on the walls of the calorimeter.

In earlier work with adsorbed nitrogen Morrison and Szasz (16) encountered anomalous effects in the region 35° to 40°K. No such effects have been found in the present work. While no attempt has been made here to reproduce the experimental conditions of the previous experiments, experience with the present apparatus now makes it seem likely that these effects were due to nitrogen being condensed in the filling tube during cooling and subsequently starting to distill back into the calorimeter around 40°K.

RESULTS

The Melting Region

The results of the heat capacity measurements in the melting region are shown in Fig. 1. The amounts adsorbed are given in terms of Vm, the volume corresponding to a completed monolayer, which had the value of 790.5 cm.^{3} at S.T.P. as deduced from a BET plot of the adsorption data at 75°K. At each concentration two sets of heat capacity measurements were made and the reproducibility may be judged from Fig. 1. The data for bulk nitrogen have been taken from the work of Giauque and Clayton (7). An interesting question is whether the heat capacity is in fact a continuous function of the temperature through the melting region. That it is within the limits of the experiments may best be seen from Fig. 2 where a heat content function is plotted. Also from Fig. 2 the upper

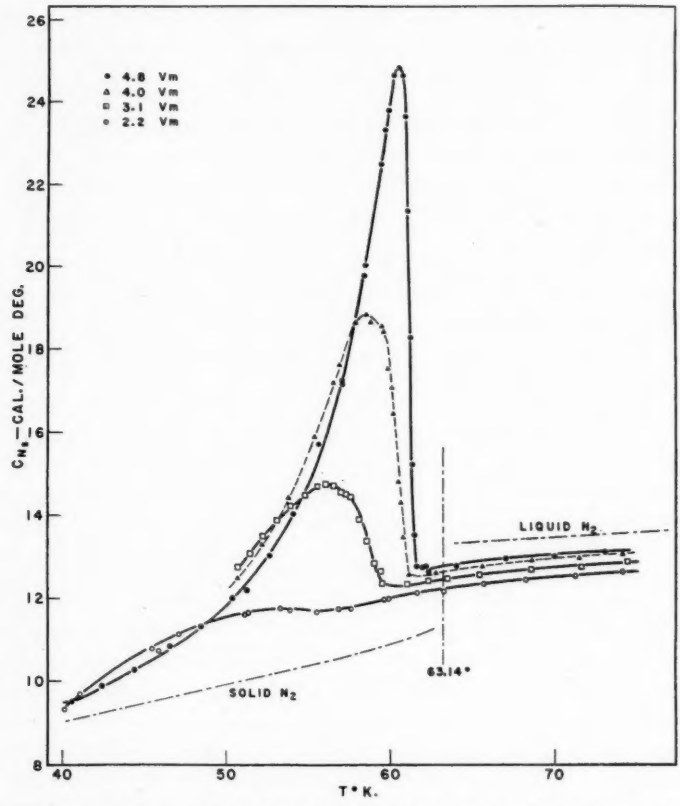

FIG. 1. The molar heat capacity of adsorbed nitrogen in the melting region. (C_{N_s} = the molar heat capacity at constant amount adsorbed.)

limits on the temperature of the melting phenomenon may be obtained and these are given in Table I.

Since the effect of the surface melting process on the general thermodynamic properties of an adsorbed system is not always appreciated it is perhaps worth while to consider the change in the isosteric heat of adsorption* and in the differential molar entropy through the melting region. The values of q_{st} as a function of the volume adsorbed were determined calorimetrically at 75°K. and values at selected volumes adsorbed at lower temperatures were calculated using the differential molar heat content deduced from the data of Fig. 2. For some reason, as yet unexplained, the experimental uncertainty in the determinations of q_{st} for nitrogen at volumes adsorbed greater than $3Vm$ was twice to three times that in the determinations of q_{st} for argon in the same region. There was

**The isosteric heat of adsorption may be defined as the difference between the differential molar heat contents of the adsorbed and gaseous phases (10). It occurs in the Clausius–Clapeyron type relation* $(\partial \ln P/\partial T)_{N_s} = q_{st}/RT^2$.

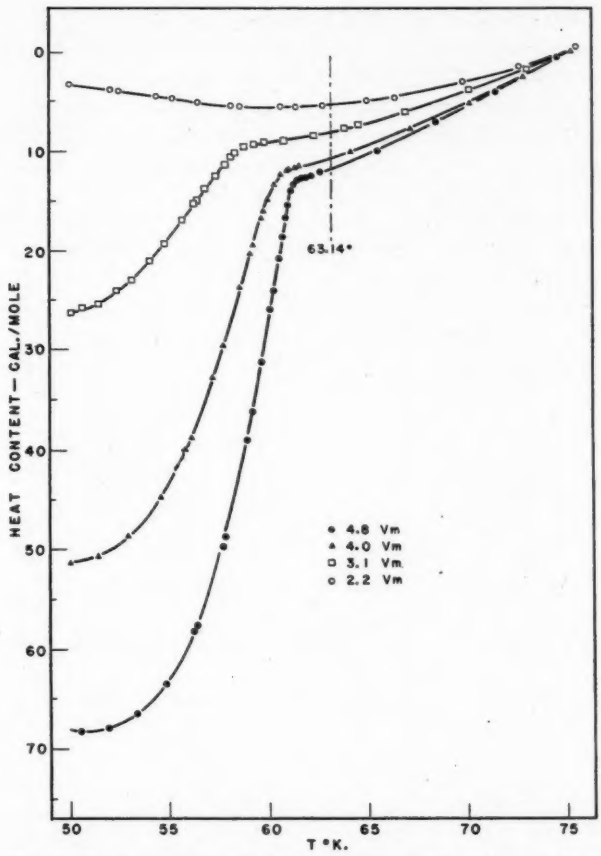

FIG. 2. The heat content of adsorbed nitrogen in the melting region. Ordinate $= \int_T^{75} C_{N_S} dT - 12(75 - T)$.

no systematic difference between values of q_{st} obtained by adsorption and by desorption. At the same time the apparent equilibrium pressures determined on adsorption and on desorption differed by about 1%. On the other hand the

TABLE I

UPPER TEMPERATURE LIMIT OF THE MELTING OF ADSORBED NITROGEN

$V_{ads.}$ at S.T.P., cm.^{3}	T,°K.	$P_{eq.}$, mm.
3800 (4.8 *Vm*)	61.4	56.4
3150 (4.0 *Vm*)	60.9	48.8
2450 (3.1 *Vm*)	59.7	35.6
1750 (2.2 *Vm*)	55	9

pressures measured during the heat capacity determinations lay between these apparent equilibrium pressures and were reproducible. Hence it is thought that they represent true equilibrium pressures of the system.

In Fig. 3 it is seen that at the higher temperatures q_{st} exceeds the heat of liquefaction of nitrogen, the excess depending upon the volume adsorbed. Through

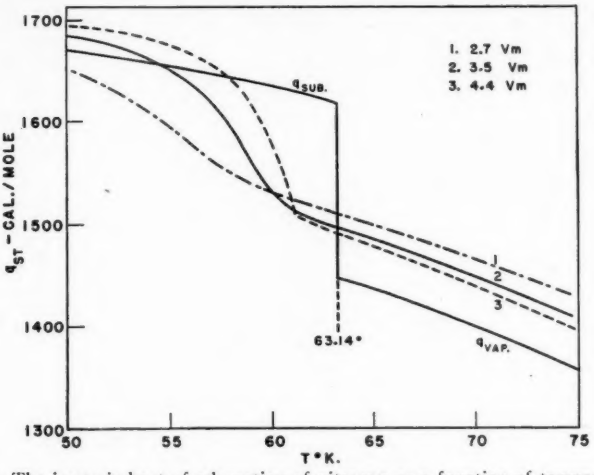

FIG. 3. The isosteric heat of adsorption of nitrogen as a function of temperature.

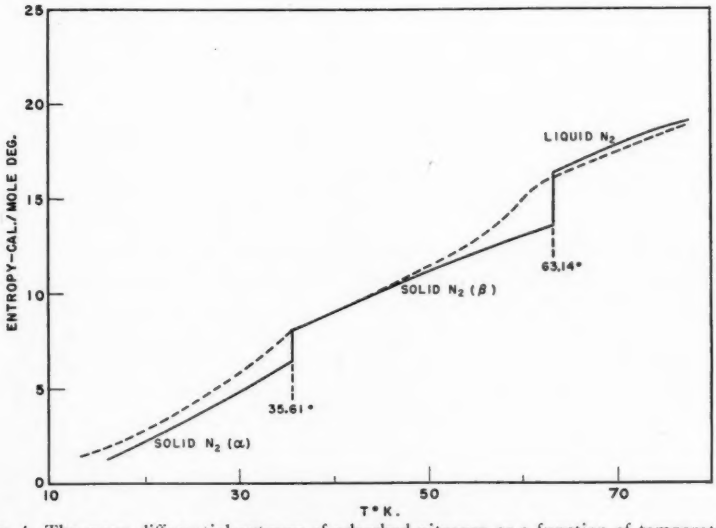

FIG. 4. The mean differential entropy of adsorbed nitrogen as a function of temperature— - - - - - $\frac{S_s(3800\ \text{cm.}^3) - S_s(1750\ \text{cm.}^3)}{2050} \times 22414$.

the melting region q_{st} increases regularly to values which in two cases are in excess of the heat of sublimation of nitrogen at the lower temperatures.

The nature of the change in the mean differential entropy with temperature is shown in Fig. 4. The calculation of the entropy below the solid transition point is questionable owing to irreversible effects which will be described in the next section; nevertheless the formal calculation was made using the heat capacity results of Series 3*A* (Fig. 7). While the mean differential molar entropy is almost identical with the entropy of solid nitrogen just above the solid transition point, it is less than the entropy of the liquid above the melting point by about 0.4 cal. per mole deg.

The adsorption isosteres which are given in Fig. 5 were computed from measurements of equilibrium pressures made in conjunction with the heat capacity determinations. To obtain the true isosteres from the measurements, correction was

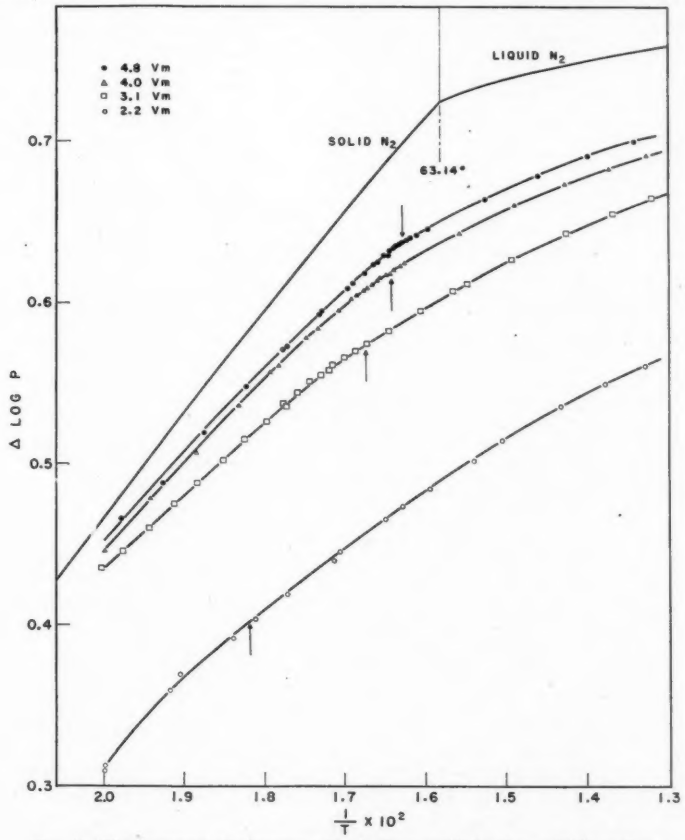

FIG. 5. The isosteres of nitrogen adsorbed on rutile in the melting region.
$\Delta \log P = \log P - 6 + 300/T$.
The arrows indicate the upper temperature limits on melting (Table I).

necessary for the gas desorbed when the temperature of the calorimeter was changed. An isotherm in the melting region was not determined because, as was noted above, there appeared to be some difficulty in reaching true equilibrium after an increment of gas was adsorbed in the calorimeter. For comparison, the isosteres of argon adsorbed on the same surface are given in Fig. 6. These results were not included in the note published previously and are pertinent to the discussion in this paper.

The Solid Nitrogen Transition Region

The heat capacity of the adsorbed nitrogen at two surface coverages (2.2 V_m

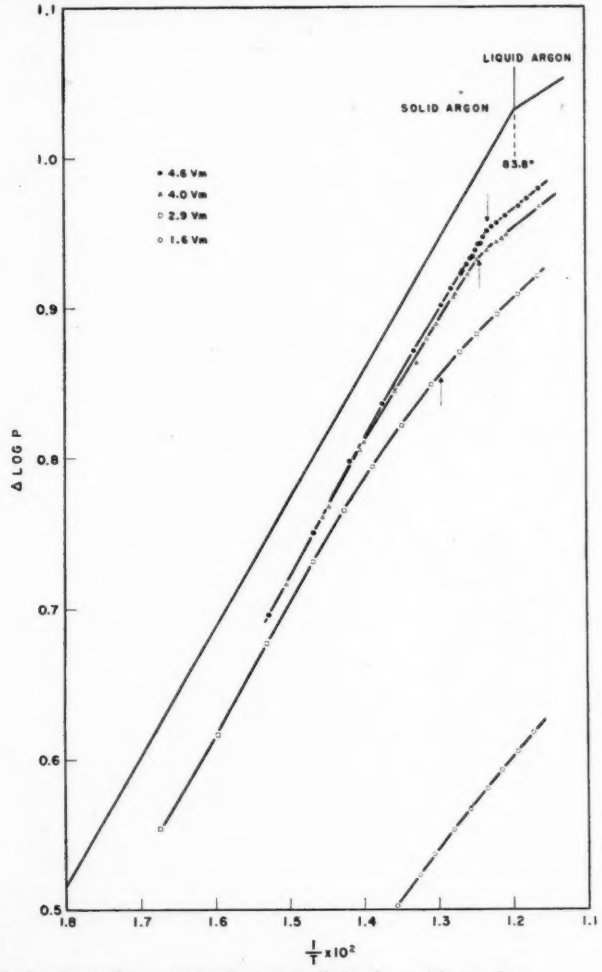

FIG. 6. The isosteres of argon adsorbed on rutile in the melting region.
$\Delta \log P = \log P - 5.5 + 320/T$.
The arrows indicate the upper temperature limits on melting as deduced from a heat content plot.

and 4.8Vm) was measured in the temperature range below 50°K. In order to simplify the diagram only the results for the higher surface coverage are shown in Fig. 7. It should be remarked, however, that the heat capacity for 2.2Vm adsorbed showed a slight hump at about 35°K. It is evident from Fig. 7 that a

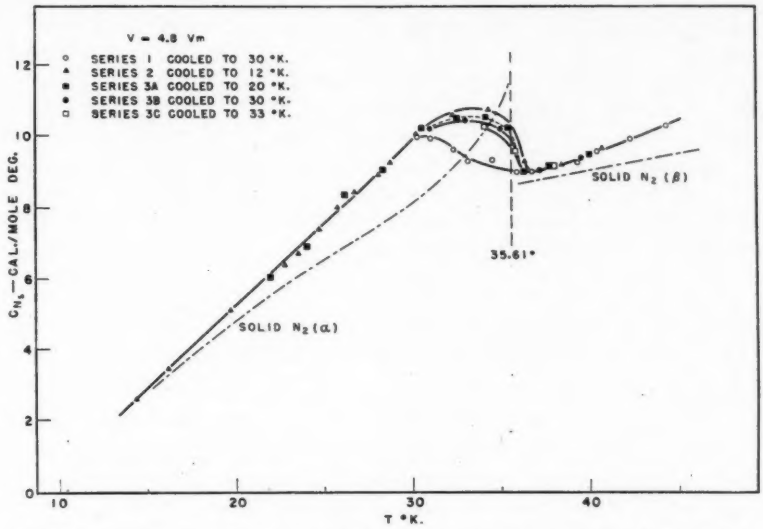
V = 4.8 Vm
SERIES 1 COOLED TO 30 °K.
SERIES 2 COOLED TO 12 °K.
SERIES 3A COOLED TO 20 °K.
SERIES 3B COOLED TO 30 °K.
SERIES 3C COOLED TO 33 °K.
SOLID N2 (α)
SOLID N2 (β)
35.61°
C Ns — CAL./MOLE DEG.
T °K.

FIG. 7. The molar heat capacity of adsorbed nitrogen in the region of the solid phase transition.

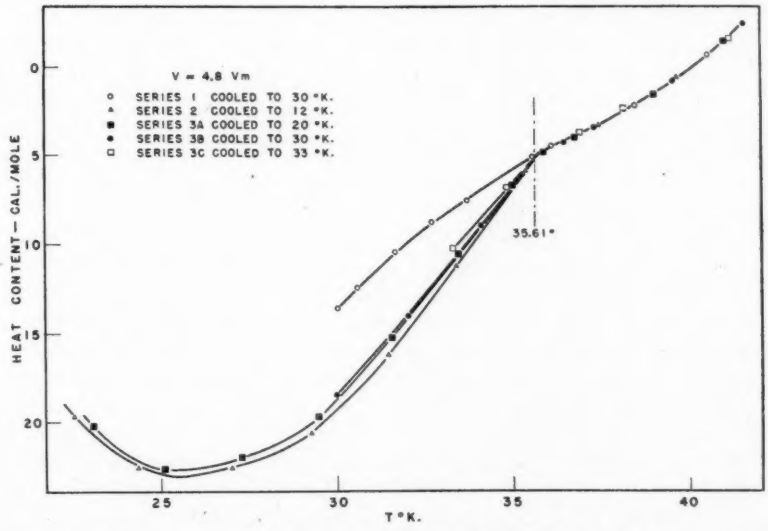
V = 4.8 Vm
SERIES 1 COOLED TO 30 °K.
SERIES 2 COOLED TO 12 °K.
SERIES 3A COOLED TO 20 °K.
SERIES 3B COOLED TO 30 °K.
SERIES 3C COOLED TO 33 °K.
35.61°
HEAT CONTENT — CAL./MOLE
T °K.

FIG. 8. The heat content of adsorbed nitrogen in the region of the solid phase transition. Ordinate = $\int_T^{40}(C_{N_s} - 8)\,dT$.

transition occurs in the temperature region where the transition in bulk solid nitrogen takes place. But there are differences to be noted between this transition and that near the normal melting point. The most important of these is that below the transition temperature the heat capacity depends upon the extent to which the system has been cooled. A similar effect has been noted by Patrick and Kemper (20) in the melting region. In the present case the system was completely reversible above 37°K., no dependence upon the nature of the cooling process being observed. In spite of this, however, heating the system to 40°K. did not appear to be sufficient to ensure reproducibility below 35°K. (compare Series 1 and Series 3*B* of Fig. 8, in which the system was cooled to 30°K. from 77°K. and from 40°K. respectively). One should also note from Fig. 8 that regardless of the extent of cooling, the upper limit of the temperature of the transition is constant at about 35.7°K. Giauque and Clayton (7) give the temperature of the transition in bulk nitrogen as 35.61°K.

DISCUSSION

Various assumptions have been made in considering the effect of surface forces on melting. Some of these will be discussed in the light of the present experiments.

1. *Bulk Solid Assumption*

In interpreting their results Patrick and Kemper (21) made the assumption that, in the freezing of an adsorbed substance, the whole available area of the solid surface was covered with a liquidlike phase of a thickness appropriate to the prevailing temperature and pressure, while the excess was present in the form of bulk solid. Higuti (9) also assumed that the solid was present in bulk form.

From this assumption it follows that until the end of the melting process the isosteres must coincide with the sublimation curve in the P,T diagram. It is at once evident that this is not true for the cases of argon and nitrogen adsorbed on rutile (Figs. 5 and 6). Also the heat capacity results for nitrogen below 50°K. (Fig. 7) show clearly that bulk solid nitrogen is not present on the surface. Any satisfactory theory of the phase transition must give the proper course of the experimental isosteres, so on this ground the assumption of bulk solid is inadequate. Nevertheless, it is worth pointing out that the bulk solid assumption does permit a quantitative calculation of the heat capacity of the adsorbed phase in the melting region to be made, and the result is roughly in accord with observation. To illustrate this, we take the example of adsorbed argon. In order to perform the calculation, it is necessary to estimate the isotherms of the liquidlike phase in the two phase region. This was done by assuming that the relative pressure with respect to liquid is independent of the temperature at a given surface coverage. For the argon results this was a good approximation because a complete adsorption isotherm was determined at 85° (5), which is very close to the melting point. For nitrogen, however, the isotherm was determined at 75°K., and there not as reliably, so that a similar calculation for nitrogen is of doubtful quality. The calculated heat capacities of adsorbed argon are shown in Fig. 9. The upper temperature limits of the melting may be compared with the experimental values of 81.3°, 80.5°, and 77.3°K. for volumes adsorbed of 4.6 *Vm*, 4.0 *Vm*, and

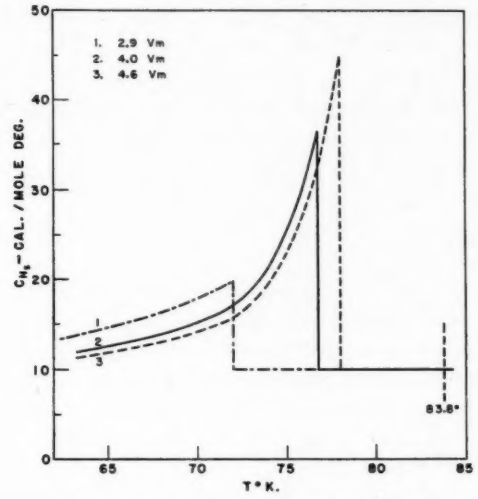

FIG. 9. The heat capacity of adsorbed argon in the melting region, calculated assuming a bulk solid phase.

2.0 *Vm* respectively. This calculation is essentially that done by Patrick and Kemper (21), who used the Patrick equation to obtain isotherms of the liquidlike phase below the melting point.

2. *Two Surface Phase Assumption*

A logical step to improve upon the postulate of bulk solid is to assume that the solid is a surface phase, i.e. that during the "melting" process two surface phases are present. The thermodynamic consequences of this assumption have been deduced by Hill (10) and by Meyer and Long (15), who have also considered second order transitions in adsorbed phases.

If there exist two adsorbed phases, 1 and 2, on a uniform surface in equilibrium with a gas phase at temperature T and pressure P, the chemical potentials of all the phases must be equal, i.e.

$$\mu_G(P,T) = \mu_1(P,T,\phi) = \mu_2(P,T,\phi) \tag{1}$$

where ϕ is the surface pressure. For an infinitesimal change in the equilibrium conditions

$$\begin{aligned} d\mu_G &= -S_G dT + V_G dP \\ &= d\mu_1 = -S_1 dT + V_1 dP + A_1 d\phi \\ &= d\mu_2 = -S_2 dT + V_2 dP + A_2 d\phi \end{aligned} \tag{2}$$

where S_1, V_1, and A_1 are the molar entropy, volume, and area of phase 1, etc. Rearranging,

$$\begin{aligned} (S_G - S_1)dT - (V_G - V_1)dP &= -A_1 d\phi, \\ (S_G - S_2)dT - (V_G - V_2)dP &= -A_2 d\phi. \end{aligned} \tag{3}$$

Consequently, on eliminating $d\phi$,

$$\frac{dP}{dT}\left(\frac{\Delta V_{G1}}{A_1} - \frac{\Delta V_{G2}}{A_2}\right) = \frac{\Delta S_{G1}}{A_1} - \frac{\Delta S_{G2}}{A_2} \tag{4}$$

where $\Delta S_{G1} = S_G - S_1$, etc. (The previous assumption that the solid retains its bulk properties means that the specific area of the solid phase, say A_2, tends to zero. If this happens while A_1 remains finite, equation (4) becomes

$$\frac{dP}{dT} = \frac{\Delta S_{G2}}{\Delta V_{G2}}$$

which is the differential form of the sublimation curve.)

Equation (4) defines a single line in the P,T plane along which the two surface phases are in equilibrium. If the transition could be performed at constant ϕ, a first order phase change would be observed on crossing this line. However, in practice, experiments are done with the total area held constant and, under these conditions, the implication of the single P,T equilibrium line is that a single isostere exists in the two phase region. Some characteristic properties of an ideal system of two surface phases are illustrated in Fig. 10 for the conditions of constant ϕ and of constant A.

A comparison of the diagrams (ii)(*b*) and (iii)(*b*) of Fig. 10 with Figs. 1, 5, and 6 shows that the actual systems do not conform to this ideal behavior. For example, the experimental isosteres at constant total area have no common region. Consequently one must conclude that for the two systems studied either the two phase model is inadequate or the postulate of a uniform surface is incorrect. Although the experimental heat capacities do not show a jump corresponding to the onset of the melting process this is not necessarily inconsistent with the requirements of the two phase model. If the molar area of the solidlike phase is sufficiently small at low temperatures, the surface may never be completely covered with this phase.

It is not obvious why the assumption of a uniform surface should be invalid. While the bare solid surface is undoubtedly heterogeneous as regards adsorption (4), it is, for these experiments, covered with one or two layers of firmly bound gas which might be expected to cover up irregularities. Moreover, even if the nonuniformity persisted through more than two layers, the two phase model should still be applicable if each phase were sufficiently extensive to cover a representative portion of the surface. Nevertheless the fact remains that the experiments do not show a single P–T line as demanded by equation (4), and it seems that the separation of the surface film into two distinct phases either does not occur or occurs only on a micro scale.

3. Two Surface Phases on a Nonuniform Surface

It is useful to consider in a qualitative way what the effect of surface nonuniformity would be on the melting process. Let us suppose that the whole system is composed of elementary regions each of which behaves like the ideal homogeneous surface already discussed. Each of these regions has its characteristic isotherm, isostere, and melting curve. An isotherm or isobar for the whole assembly of regions will now show vertical segments wherever an elementary region melts. An isostere for the whole assembly will follow the melting curve of an

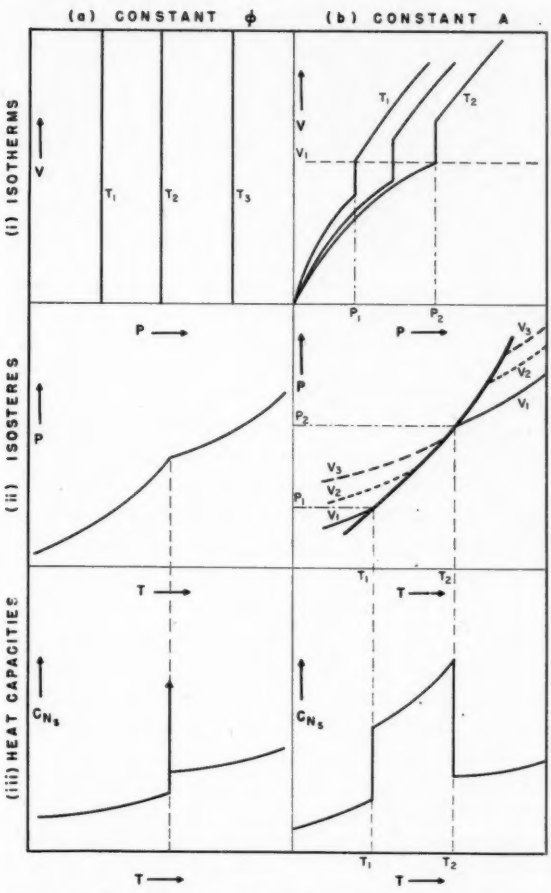

FIG. 10. Some properties of an ideal two surface phase system.

individual region which is in the process of melting at a given temperature. During the temperature intervals in which no melting is taking place, the slope of the isostere will be determined by the behavior of all the elements. Thus, in the melting region, the isosteres for an aggregate of a finite number of elementary regions will consist of a sequence of oblique steps.

Experiment gives no indication of the existence of such steps so that one is forced to conclude, on this basis, that there is a continuous distribution of areas, all having slightly different properties. The result is that the melting process is smeared out and the isosteres of the whole assembly, instead of coinciding with the melting curves of the individual elements over a certain range, cross the melting curves at an angle. The only melting curve which may be deduced with any confidence from the experimental data is that corresponding to the first onset

of solidification, which is indicated by a change in the slope of the isosteres. Presumably, this is the melting curve for that part of the surface most favorable to the formation of the solidlike phase.

It may be mentioned that equation (4) can be applied to this latter melting curve. Neglecting the volume of the adsorbed phases in comparison with that of the gas, equation (4) may be rewritten—

$$(5)^* \qquad RT\frac{d\ln P}{dT} = S_G - \frac{S_1A_2 - A_1S_2}{A_2 - A_1}.$$

If we substitute the experimental values of $d\ln P/dT$ (0.29 deg.$^{-1}$ for nitrogen and 0.18 deg.$^{-1}$ for argon) in equation (5) and assume that S_2 and S_1 are equal to the molar entropies of bulk solid and liquid respectively, we deduce $A_1/A_2 = 1.24$ for nitrogen and 1.37 for argon. It should be noted that the melting curves for other parts of the surface would yield higher values of this ratio.

Meyer and Long (15) calculated A_1 and A_2 on the assumptions (*a*) that the two adsorbed phases had the same spacing as the corresponding bulk phases and (*b*) that the average number of layers was the same in each phase. The above results show that if the assumptions about the entropies and spacing are essentially correct, the average number of layers in the solidlike phase is greater than in the liquidlike phase.

CONCLUSION

It is possible to reconcile the model of two surface phases with the experimental results by supposing that there are no macroscopic regions of the surface on which melting can proceed uniformly. However, the data presented here do not constitute conclusive proof that this is the only model applicable. It is possible that the melting process in adsorbed films does not occur by the separation of phases but by a gradual disordering process throughout the film. It is important to note that the postulate of the effect of surface nonuniformity implies a dependence of the melting process on the nature of the substrate. A comparison of the melting of the same substance on different substrates should therefore be significant. No such experimental data exist for a first order transition. The λ-transition in adsorbed films of helium has been examined on two substrates (6, 14), but the results are not of sufficient accuracy to permit a worth-while comparison.

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**Equation (7b) of Meyer and Long (15). In the derivation of their equation (7c), Meyer and Long assumed that $A_1 = A_2$. However, at the same time $S_1 = S_2$ so that in equation (7c) S_G should be replaced by $S_G - \frac{1}{2}(S_1 + S_2)$.*

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SYNTHESIS OF PYRAZOLONES FROM α-KETO AND α-CYANO ESTERS[1]

By Paul E. Gagnon, Jean L. Boivin,[2] and Alexander Chisholm[3]

ABSTRACT

1,4-Dimethyl-3-amino-5-pyrazolone and 4-methyl- and 4-ethyl-3-amino-1-phenyl-5-pyrazolones were synthesized from α-keto esters and methyl- and phenylhydrazines. The hydrazones first obtained were transformed into pyrazolones having a carbethoxy group in position 3, which was converted into an amino group by a Curtius degradation. 2,4-Dimethyl-3-amino-5-pyrazolone was obtained directly from methylhydrazine and ethyl α-cyanopropionate. A series of 3-imino-2-methyl-5-pyrazolones monosubstituted in position 4 with pentyl, hexyl, heptyl, and octyl groups and another series disubstituted in position 4 with butyl, hexyl, and heptyl groups were also prepared from the corresponding mono- and disubstituted cyanoacetates and methylhydrazine.

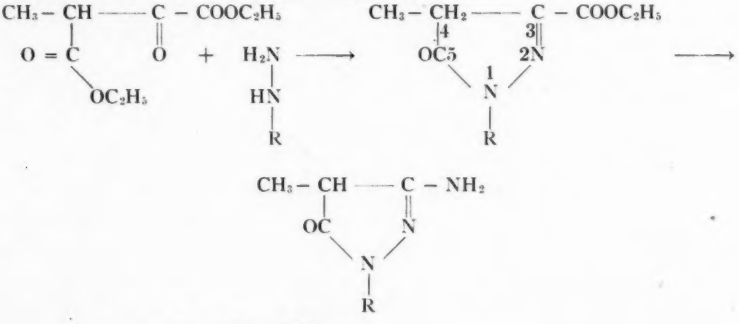
The ultraviolet absorption spectra were determined in neutral and acid medium.

INTRODUCTION

Pyrazolones prepared from ethyl mono- or disubstituted cyanoacetates and hydrazine have been previously reported (4, 6). Phenylhydrazine, semicarbazide, and N-benzoylhydrazine were condensed in the same way to yield corresponding 2-phenyl-, 2-carboxamido-, and 2-benzoyl-5-pyrazolones (1, 2, 4).

The main object of the present work was to study the condensation of methylhydrazine and phenylhydrazine with α-keto and α-cyano esters with a view of better establishing the constitution of pyrazolones.

Ethyl α-ethoxyalylpropionate was reacted with methyl- and phenylhydrazine to yield the corresponding hydrazones which upon heating were transformed into pyrazolones. A Curtius degradation of the 3-carbethoxy groups was made through the hydrazides, azides, and urethanes. The hydrolysis of the urethanes yielded the 4-methyl-3-amino-1-substituted-5-pyrazolones.



R = CH_3 or C_6H_5

[1] *Manuscript received July 15, 1952.*

Contribution from the Department of Chemistry, Laval University, Quebec, Que. This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.

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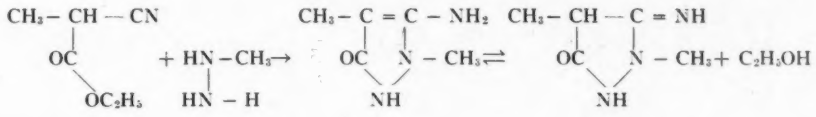
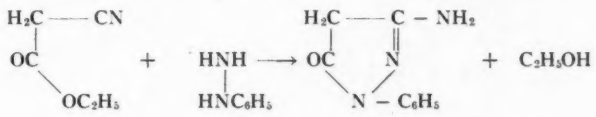
Ethyl α-ethoxalylbutyrate was reacted with phenylhydrazine in the same way, yielding 4-ethyl-3-amino-1-phenyl-5-pyrazolone.

Ethyl α-cyanopropionate was heated with methylhydrazine and gave 2,4-dimethyl-3-amino-5-pyrazolone. The properties of this compound, for instance, its melting point and ultraviolet absorption spectrum, were quite different from those of 1,4-dimethyl-3-amino-5-pyrazolone prepared from ethyl α-ethoxalylpropionate and methylhydrazine.

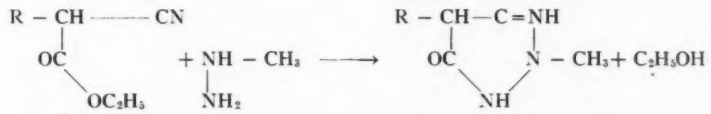
It is of interest to note that when an ethyl α-substituted-cyanoacetate is heated with methylhydrazine, a pyrazolone having a substituent in position 2 and not in position 1 is formed. Methylhydrazine thus behaves like phenylhydrazine (4).



It has been previously reported that when unsubstituted ethyl cyanoacetic ester reacted with methylhydrazine (7) and phenylhydrazine (10), pyrazolones having a methyl or phenyl group in position 1 and not in position 2 were formed.



By treating other ethyl cyanoacetates α-substituted with pentyl, hexyl, heptyl, and octyl groups with methylhydrazine sulphate in the presence of sodium ethylate, 4-monosubstituted-3-imino-2-methyl-5-pyrazolones were prepared.



With methylhydrazine sulphate under similar conditions, ethyl cyanoacetates α-disubstituted with butyl, hexyl, and heptyl groups yielded 4,4-disubstituted-3-imino-2-methyl-5-pyrazolones.

The individual properties and analyses of all the pyrazolones prepared are given in Tables I and II.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of the pyrazolones were determined in neutral and acid solution by a method already described (4) and the results obtained are summarized in Tables I and II and Figs. 1 to 5.

1,4-Dimethyl-3-amino-5-pyrazolone, in which the positions of the methyl

TABLE I

4-MONOSUBSTITUTED-3-SUBSTITUTED-1- or 2-SUBSTITUTED-5-PYRAZOLONES

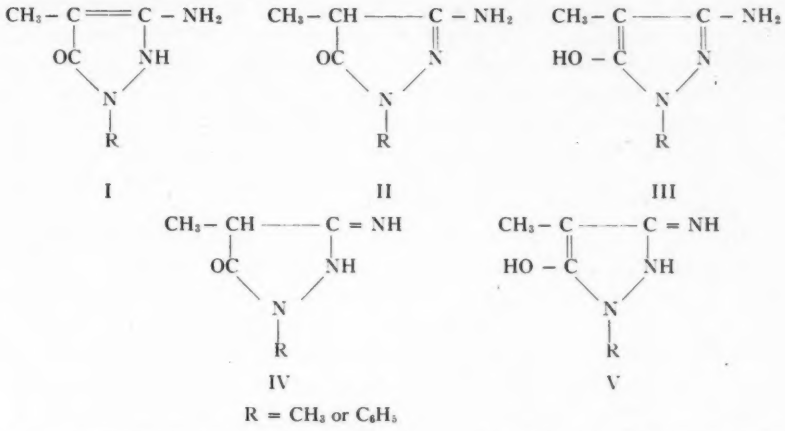
Substituents				Formula	M.p., °C.	Analysis		Ultraviolet absorption maxima			
						Nitrogen, %		Neutral		Acid	
4	3	2	1			Calc.	Found	Å	log E_m	Å	log E_m
CH_3	$COOC_2H_5$		CH_3	$C_8H_{12}O_3N_2$	150–151	15.2	15.3				
CH_3	$NHCOOC_2H_5$		CH_3	$C_8H_{13}O_3N_3$	250–251	21.1	20.6				
CH_3	NH_2		CH_3	$C_5H_9ON_3$	140–141	33.0	32.8	2500 2860	3.48 3.20	2400	3.48
CH_3	$CONHNH_2$		C_6H_5	$C_{11}H_{12}O_2N_4$	179–180	24.1	22.6				
CH_3	$NHCOOC_2H_5$		C_6H_5	$C_{12}H_{13}O_3N_3$	242–244	16.1	16.2				
CH_3	NH_2		C_6H_5	$C_{10}H_{11}ON_3$	137–138	22.1	21.8	2520	4.22	2500	4.14
C_2H_5	$COOC_2H_5$		C_6H_5	$C_{14}H_{16}O_3N_2$	199–200	11.2	10.7				
C_2H_5	$CONHNH_2$		C_6H_5	$C_{12}H_{14}O_2N_4$	144–145	22.8	22.5				
C_2H_5	$NHCOOC_2H_5$		C_6H_5	$C_{14}H_{17}O_3N_3$	202–203	15.3	15.4				
C_2H_5	NH_2		C_6H_5	$C_{11}H_{13}ON_3$	145–146	20.7	20.6	2520	4.01	2500	4.18
CH_3	NH_2	CH_3		$C_5H_9ON_3$	223–224	33.0	33.2	2520 2860	3.94 3.36	2400	3.93

TABLE II

4-MONO- AND 4,4-DISUBSTITUTED-3-IMINO-2-METHYL-5-PYRAZOLONES

4-Mono-	4,4-Di-	M.p., °C.	Formula	Analysis		Ultraviolet absorption maxima			
				Nitrogen, %		Neutral		Acid	
				Calc.	Found	Å	log E_m	Å	log E_m
C_5H_{11}		85–86	$C_9H_{13}ON_3$	22.9	22.4	2840	3.66	2840	3.45
C_6H_{13}		101–103	$C_{10}H_{15}ON_3$	21.3	20.6	2850	3.48	2800	3.44
C_7H_{15}		79–80	$C_{11}H_{17}ON_3$	19.9	19.5	2840	3.08	2760	3.08
C_8H_{17}		86–87	$C_{12}H_{19}ON_3$	18.6	18.4	2850	3.52	2850	3.55
	$(C_4H_9)_2$	141–143	$C_{12}H_{23}ON_3$	18.6	18.4	2700	3.60	2650	3.62
	$(C_6H_{13})_2$	188–190	$C_{16}H_{31}ON_3$	14.9	15.1	2740	3.68	2670	3.68
	$(C_7H_{14})_2$	135–136	$C_{18}H_{35}ON_3$	13.6	13.5	2720	3.48	2650	3.63

groups are fixed by the method used to prepare the compound, may exist in five possible tautomeric forms:



I II III

IV V

R = CH_3 or C_6H_5

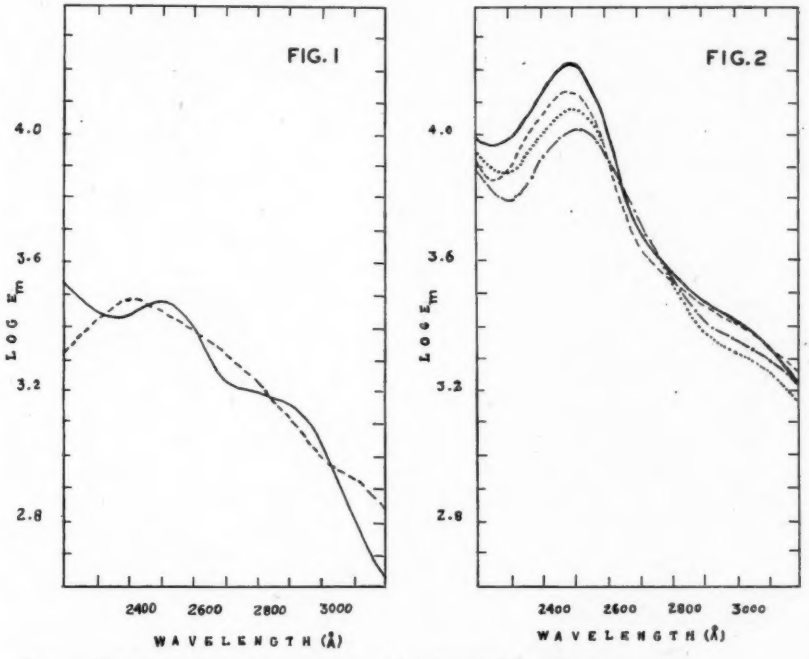


FIG. 1. Ultraviolet absorption spectrum of 1,4-dimethyl-3-amino-5-pyrazolone: ———— in neutral solution, – – – – – in acid solution.

FIG. 2. Ultraviolet absorption spectrum of 4-methyl-3-amino-1-phenyl-5-pyrazolone: ———— in neutral solution, – – – – – in acid solution; and of 4-ethyl-3-amino-1-phenyl-5-pyrazolone: – · – · – in neutral solution, ····· in acid solution.

Stenzel showed that the substituent in position 4 could determine whether the 3-substituent was an amino or imino group and that 4-alkyl-3-amino-2-methyl-1-phenyl-5-pyrazolones were present largely in the amino form (9). It has also been shown that pyrazolones with a low absorption maximum at high wave length probably have a 2:3 double bond (structure II) or an imino group in position 3 and that those with a high maximum at short wave length probably have the 3:4 ethylenic bond (structure I)(1, 4, 5).

It was also found that in alkaline solution pyrazolones exist as form III (3, 4). In neutral and acid solution, however, the structure probably varies according to the substituents.

1,4-Dimethyl-3-amino-5-pyrazolone (Fig. 1) has two ultraviolet absorption maxima in neutral solution, a low one at long wave length and a higher one at short wave length. On acidification, the low one disappears and the high one is shifted to shorter wave length which is indicative of the presence of an amino group (8). Then, from what has previously been said, one may conclude that it exists as the two forms I and II in neutral solution and only as form I in acid medium.

4-Methyl- and 4-ethyl-3-amino-1-phenyl-5-pyrazolones may exist in five struc-

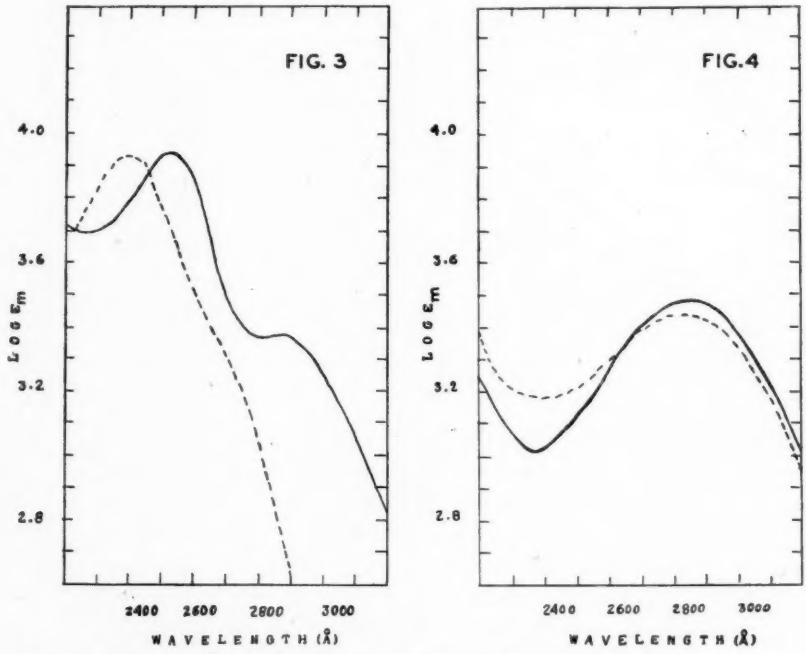
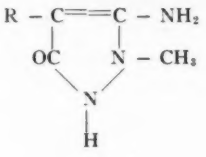


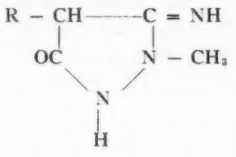
FIG. 3. Ultraviolet absorption spectrum of 2,4-dimethyl-3-amino-5-pyrazolone:
———— in neutral solution, – – – – – – in acid solution.
FIG. 4. Ultraviolet absorption spectrum of 4-*n*-hexyl-3-imino-2-methyl-5-pyrazolone:
———— in neutral solution, – – – – – – in acid solution.

tures, like the 1,4-dimethyl compound. However, comparison of their ultraviolet absorption spectra (Table II) (Fig. 2) with those of the 4-methyl- and 4-ethyl-3-amino-2-phenyl-5-pyrazolones, already described (4), reveals that they probably have the 3:4 ethylenic bond (structure I) in neutral solution. They have a single high maximum at short wave length which corresponds almost exactly with that of the 2-phenyl-5-pyrazolones just mentioned and since these latter compounds must exist with the 3:4 ethylenic structure, the 1-phenyl compounds probably do also. The difference in behavior between the 1-phenyl compounds with one maximum and the 1,4-dimethyl compound with two maxima may be ascribed to the ability of the phenyl group to withdraw electrons from the ring.

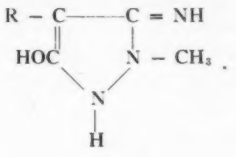
2,4-Dimethyl-3-amino-5-pyrazolone (Fig. 3) may have the following structures:



VI



VII



VIII

R = CH_3

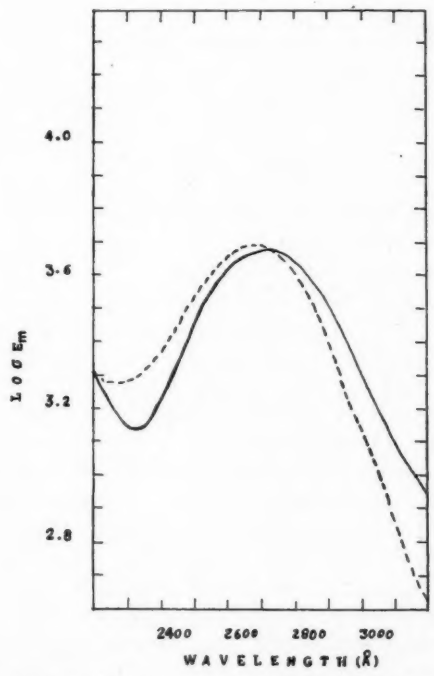
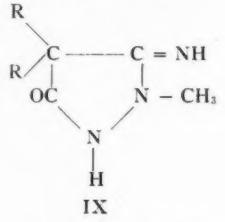


FIG. 5. Ultraviolet absorption spectrum of 4,4-di-*n*-hexyl-3-imino-2-methyl-5-pyrazolone: ———— in neutral solution, – – – – – – in acid solution.

Pyrazolones were previously shown to exist in the hydroxyl form (VIII) in alkaline media (4). In neutral solution, 2,4-dimethyl-3-amino-5-pyrazolone exhibited two maxima in its ultraviolet absorption spectrum, which suggested that the two forms VI and VII were present. On acidification, one maximum disappeared. The maximum which remained was a high intensity maximum at short wave length. This type of curve has been previously assigned to pyrazolones with a 3:4 ethylenic bond. Since the 2:3 unsaturated compound can not exist, the 3:4 unsaturated form must be present and the imino form (VII), which is known to give the observed low maximum, must be postulated as the form that disappears.

4-Monosubstituted-3-imino-2-methyl-5-pyrazolones (VII; R = C_5H_{11}, C_6H_{13}, C_7H_{15}, or C_8H_{17}) (Fig. 4) are formulated as having an imino group, which confirms results previously obtained (2). The low maximum in the ultraviolet absorption spectrum of these compounds suggests that either they have a 2:3 double bond or an imino group in position 3, but since they cannot have a stable 2:3 double bond, being substituted in position 2, they must have the imino form.

4,4-Disubstituted-3-imino-2-methyl-5-pyrazolones (Fig. 5) certainly have the following structure (IX) in neutral or acid solution since no other one is possible.



IX

R = C_4H_9, C_6H_{13}, or C_7H_{15}.

Their single low intensity absorption maximum indicates that the imino group is present.

Differences and Analogies of the Pyrazolones

A close examination of Tables I and II, where the properties and analyses of the different pyrazolones prepared are given, readily indicates their differences and analogies.

For instance, 1,4-dimethyl-3-amino-5-pyrazolone and 2,4-dimethyl-3-amino-5-pyrazolone have the melting points 140° to 141°C. and 223° to 224°C. and the intensities of the maxima found at the same wave length are 3.48 and 3.94 respectively in neutral medium and 3.48 and 3.93 at 2400 Å in acid medium. The two pyrazolones both have a double bond between the two carbons 3 and 4.

4-Methyl-3-amino-1-phenyl-5-pyrazolone and 4-ethyl-3-amino-1-phenyl-5-pyrazolone melt at 137° to 138°C. and 145° to 146°C. and the intensities of the maxima in neutral medium at 2520 Å are 4.22 and 4.01 respectively whereas in acid solution they are practically equal, being 4.14 and 4.18, at 2500 Å. This shows that the 4-methyl and 4-ethyl radicals have no great influence on the rest of the molecule.

From Table II one easily sees that the maxima are found at longer wave length,

about 2850 Å, for the 4-monosubstituted-3-imino-2-methyl-5-pyrazolones than they are for the 4,4-disubstituted-3-imino-2-methyl-5-pyrazolones, 2720 Å. The intensities of the maxima however do not differ considerably.

EXPERIMENTAL*

All the pyrazolones were prepared by treatment of esters with hydrazine, methylhydrazine, or phenylhydrazine. Their properties are listed in Tables I and II.

Most of them were obtained as viscous liquids. Some solidified on standing for some time but since very few could be purified by ordinary methods it was necessary to use chromatography.

The apparatus was a 1 liter cylinder (6 × 45 cm.) with a large cork fitted with a wire holder for the filter paper strip. Inside the cylinder was a 50 ml. beaker which contained one of the solvents. The filter paper strips were 50 cm. long and 3 cm. wide. The solvents used were petroleum ether (b.p. 65–110°C.) and water. Other solvent pairs such as *n*-butanol–water and diethyl ether – water were tried, but with no success. One solvent, usually petroleum ether, was placed in the beaker and the other outside it and the system was allowed to remain undisturbed for about an hour to reach equilibrium. The impure solid material (about 0.02 gm.) was then placed on the filter paper strip, which was suspended with one end in the solvent in the beaker, the material itself being 2 to 5 cm. above the liquid level. The time necessary for purification varied with the materials and the solvents used from four hours to several days. When the separation was complete, the paper was removed from the solvent and allowed to dry. The compound was recovered at the original point of application, but impurities had diffused upward on the paper so that frequently a perfectly white substance with sharp melting point was obtained which could then be recrystallized in a normal manner, or could be sublimed. Sublimation when possible was the best method of purification. It was carried out under specific conditions of temperature and pressure for each substance.

1,4-Dimethyl-3-carbethoxy-5-pyrazolone

To methylhydrazine (4.6 gm., 0.1 mole) was added ethyl α-ethoxyalylpropionate (20.2 gm., 0.1 mole). The mixture was heated for one hour at 110°C., then for two hours at 170°C. A dark red viscous liquid was obtained. Yield, 14.2 gm. (76%). The liquid was dissolved in a dilute solution of potassium hydroxide (10%). The solution, after extraction with ether, was acidified with dilute acetic acid (33%). The acidic solution was then extracted with ether. The ethereal solution was dried over anhydrous calcium chloride. The ether was distilled off and a solid material was obtained which was chromatographed. The white solid from the chromatogram was sublimed at 140°C. (2 mm.): m.p. 150–151°C. Calc. for $C_8H_{12}O_3N_2$: N, 15.2%. Found: N, 15.3%.

1,4-Dimethyl-3-carbethoxyamino-5-pyrazolone

To boiling hydrazine hydrate (1.0 gm., 0.02 mole) was added 1,4-dimethyl-3-carbethoxy-5-pyrazolone (3.0 gm., 0.016 mole). The mixture was heated at 130°C.

**All melting points were taken on a Dennis melting point apparatus.*

until evolution of vapors ceased. The residue was dissolved in concentrated hydrochloric acid and the solution was cooled to − 10°C. in an ice–salt bath. A concentrated solution of sodium nitrite was added until starch–iodide test paper gave a positive test for nitrite ion. The cold solution was extracted with ether, and the ethereal extract was dried over anhydrous calcium chloride. The ether was removed under reduced pressure leaving a brown viscous liquid (0.7 gm.) which was dissolved in alcohol. The solution was refluxed for three hours. After the solution had been allowed to stand for several days, a small amount of 1,4-dimethyl-3-carbethoxyamino-5-pyrazolones was obtained: m.p. 250 to 251°C. Yield, 0.3 gm. (10%). Calc. for $C_8H_{13}O_3N_3$: N, 21.1%. Found: N, 20.6%.

1,4-Dimethyl-3-amino-5-pyrazolone

1,4-Dimethyl-3-carbethoxyamino-5-pyrazolone (0,4 gm., 0.002 mole) was refluxed in dilute sodium hydroxide (10%) for 18 hr. On neutralization to pH 7 with hydrochloric acid, a large volume of inorganic material precipitated. This was removed by filtration. The filtrate was acidified with dilute acetic acid (33%), extracted with ether, and evaporated to dryness. A yellow residue was obtained which contained much inorganic material. It was chromatographed. The material on the paper was extracted with alcohol, and on evaporation of the alcohol a solid precipitated: m.p. 140 to 141°C. Calc. for $C_5H_9ON_3$: N, 33.0%. Found: N, 32.8%.

4-Methyl-3-carboxyhydrazide-1-phenyl-5-pyrazolone

4-Methyl-3-carbethoxy-1-phenyl-5-pyrazolone (11) sublimed at 140°C. (20 mm.): m.p. 151 to 152°C. (1.8 gm., 0.007 mole) was added to boiling hydrazine hydrate (5 ml., 0.1 mole) in a 50 ml. round-bottom flask. The mixture was refluxed for one hour, left in a vacuum desiccator over calcium chloride for 12 hr., and then recrystallized from ethanol. A white crystalline product was obtained. Yield, 1.4 gm. (83%). This compound was sublimed at 140 to 150°C. (20 mm.): m.p. 179 to 180°C. Calc. for $C_{11}H_{12}O_2N_4$: N, 24.1%. Found: 22.6%.

4-Methyl-3-carbethoxyamino-1-phenyl-5-pyrazolone

4-Methyl-3-carbethoxy-1-phenyl-5-pyrazolone (11) (5 gm., 0.02 mole) was added to hydrazine hydrate (5.5 ml., 0.11 mole). The mixture was heated at 120°C. until complete solution of the solid was obtained. The solution was then cooled and acidified with acetic acid; a precipitate appeared. An excess of hydrochloric acid was added to dissolve the precipitate. The acid solution was cooled to 0°C. in an ice bath and a concentrated solution of sodium nitrite was added during mechanical stirring. When the diazotization was complete, as shown by the starch–iodide paper test, the solution was extracted with ether. The ethereal solution was washed with water, then with a dilute (10%) sodium bicarbonate solution, with water again, and was dried over calcium chloride. The ether was removed under reduced pressure, which cooled the flask and induced crystallization of a low melting product which deflagrated: m.p. 60 to 65°C. This product, the azide, was dissolved in absolute ethanol and refluxed on a steam bath. When the evolution of nitrogen was complete, a white solid material separated from the solution: m.p. 242 to 244°C. Yield, 1.5 gm. (28%). The urethane decomposed at

170°C. (20 mm.) but at 170°C. (1 mm.) it was possible to sublime it. Calc. for $C_{13}H_{15}O_3N_3$: N, 16.1%. Found: N, 16.2%.

4-Methyl-3-amino-1-phenyl-5-pyrazolone

4-Methyl-3-carbethoxyamino-1-phenyl-5-pyrazolone (10 gm.) was refluxed with concentrated hydrochloric acid for 30 min., then with dilute (20%) hydrochloric acid for six hours. The suspension was allowed to stand for 18 hr. The solid obtained was unchanged urethane, which was then refluxed with dilute (10%) sodium hydroxide for 18 hr. The reaction proceeded with formation of a dark solution. On completion of the hydrolysis, the alkaline solution was filtered and acidified with dilute (33%) acetic acid. A brown amorphous material precipitated and there was evolution of a gas. The solid was recrystallized from dilute alcohol: m.p. 137 to 138°C. Calc. for $C_{10}H_{11}ON_3$: N, 22.1%. Found: N, 21.3%.

4-Ethyl-3-carbethoxy-1-phenyl-5-pyrazolone

Ethyl α-ethoxalylbutyrate (21 gm., 0.1 mole) (11) was mixed with phenylhydrazine (11 gm. 0.11 mole) and the mixture was heated on a steam bath for an hour and in an air bath at 170 to 190°C. for 90 min. The material was dissolved in alcohol and the solution poured into dilute alkali. The alkaline solution was filtered, some insoluble viscous materials were thus removed, and the filtrate was acidified with acetic acid. The ester precipitated was redissolved in dilute alkali and reprecipitated: m.p. 199 to 200°C. Yield, 6 gm. (21%). Calc. for $C_{13}H_{16}N_2O_3$: N, 11.29%. Found: N, 10.7%.

4-Ethyl-3-carboxyhydrazido-1-phenyl-5-pyrazolone

To boiling hydrazine hydrate (10 ml., 0.3 mole) was added pure dry 4-ethyl-3-carbethoxy-1-phenyl-5-pyrazolone (6 gm., 0.023 mole). The mixture was heated at 125°C. for 90 min. At the end of this time, a straw-colored liquid was obtained which quickly solidified on cooling. The product was recrystallized from water: m.p. 144 to 145°C. Yield, 4.4 gm. (90%). Calc. for $C_{12}H_{14}O_2N_4$: N, 22.8%. Found: N, 22.5%.

4-Ethyl-3-carbethoxyamino-1-phenyl-5-pyrazolone

4-Ethyl-3-carboxyhydrazido-1-phenyl-5-pyrazolone (2 gm., 0.008 mole) was dissolved in concentrated hydrochloric acid. The clear yellow solution was cooled to 0°C. and a concentrated solution of sodium nitrite was added until starch–iodide paper turned blue when tested with a drop of the solution. A yellow solid that deflagrated violently on heating precipitated: m.p. 53 to 54°C. Yield, 1.5 gm. (72%). The azide obtained (0.9 gm., 0.035 mole) was refluxed with absolute ethanol for an hour. It dissolved and on further heating a pale yellow solid precipitated. Yield, 0.5 gm. (53% based on the azide). The urethane was sublimed at 200°C. (2 mm.): m.p. 202 to 203°C. Calc. for $C_{14}H_{17}O_3N_3$: N, 15.3%. Found: 15.4%.

4-Ethyl-3-amino-1-phenyl-5-pyrazolone

4-Ethyl-3-carbethoxyamino-1-phenyl-5-pyrazolone (0.5 gm., 0.018 mole) was treated with dilute (10%) sodium hydroxide and the mixture was refluxed for two hours, cooled, filtered, and acidified with dilute (33%) acetic acid. The brown

precipitate thrown out of solution was purified by crystallization from dilute alcohol: m.p. 145 to 146°C. Very nearly quantitative yield was obtained from the hydrolysis. Calc. for $C_{11}H_{13}ON_3$: N, 20.7%. Found: N, 20.6%.

2,4-Dimethyl-3-amino-5-pyrazolone

Ethyl α-cyanopropionate (12.7 gm., 0.1 mole) was added to methylhydrazine (4.6 gm., 0.1 mole) and the resulting mixture was stirred. Heat was evolved. The material was allowed to stand overnight and a precipitate formed. The solid was filtered off and washed with ether. A sticky brown solid was obtained. This solid was chromatographed and a yellow powder was recovered: m.p. 215 to 216°C. It was sublimed at 200°C. (1 mm.): m.p. 223 to 224°C. Calc. for $C_5H_9ON_3$: N, 33.1%. Found, N, 33.2%.

4-Alkyl-3-imino-2-methyl-5-pyrazolone

Mixtures of ethyl monosubstituted cyanoacetates (0.1 mole) and methylhydrazine sulphate (0.1 mole) were added to solutions of sodium (0.3 mole) in absolute ethanol (100 ml.). After the solutions were refluxed for 18 hr., the alcohol was evaporated under reduced pressure and the residues dissolved in water. The solutions were extracted with ether to remove unreacted starting materials, and the aqueous layers were acidified with acetic acid (33%). Viscous liquids separated from the solutions and solidified on long standing over phosphorus pentoxide. These products were chromatographed and the materials from the chromatograms were further purified by crystallization from dilute alcohol.

The 4-alkyl-3-imino-2-methyl-5-pyrazolones prepared are listed, together with their melting points, analyses, and ultraviolet absorption spectrophotometric data in Table II.

4,4-Dialkyl-3-imino-2-methyl-5-pyrazolones

Ethyl dialkyl instead of monoalkyl cyanoacetates were treated with methyl hydrazine sulphate just as indicated for the 4-alkyl-3-imino-2-methyl-5-pyrazolones.

The 4,4-disubstituted-3-imino-2-methyl-5-pyrazolones obtained are listed together with their melting points, analyses, and ultraviolet spectrophotometric data in Table II.

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Contents

Page

A Spectroscopic Study of Hydrogen Bonding in Performic and Peracetic Acids—*Paul A. Giguère and A. Weingartshofer Olmos* - 821

The Size and Shape of Lysozyme—*J. Ross Colvin* - - - - - - 831

Addition Compounds of the Group IV Halides. I. Triethylamine and the Tetrachlorides of Silicon, Germanium, Tin, and Titanium—*W. R. Trost* - - - - - - - - - - - - - - - - - - - 835

Addition Compounds of the Group IV Halides. II. Ethylamine and the Tetrachlorides of Silicon, Germanium, Tin, and Titanium—*W. R. Trost* - - - - - - - - - - - - - - - - - - - 842

Synthesis of 2-Methyl-C^{14}-1,4-naphthoquinone——*R. V. Phillips, L. W. Trevoy, L. B. Jaques, and J. W. T. Spinks* - - - - - 844

Density Distributions in a Vertical Tube Containing Xenon Near the Critical Temperature as Measured by a Radioactive Tracer Technique—*M. A. Weinberger and W. G. Schneider* - - - - 847

The Action of Hydroxylamine, its o-Methyl Ether, and Their Hydrochlorides on Cellulose Trinitrate in Pyridine—*G. H. Segall and C. B. Purves* - - - - - - - - - - - - - - - - - - - 860

Structure of a Levan Produced by *Bacillus polymyxa*—*Diarmuid Murphy* - 872

The Decomposition of Hypochlorous Acid—*M. W. Lister* - - - - 879

Phase Transitions in Multimolecular Layers of Adsorbed Nitrogen—*J. A. Morrison, L. E. Drain, and J. S. Dugdale* - - - - - - 890

Synthesis of Pyrazolones from α-Keto and α-Cyano Esters—*Paul E. Gagnon, Jean L. Boivin, and Alexander Chisholm* - - - - 904

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